UNIVERSITY OF BOTSWANA

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HYDROGEOCHEMISTRY OF THE KASANE THERMAL SPRING, BOTSWANA

BY

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A thesis submitted in partial fulfilment of the requirements for the Degree of Master of Science in Hydrogeology

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Gaborone

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Finally, to my heavenly Father who by Him all things are possible, I am truly grateful.

ABSTRACT

The hydrogeochemistry of the Kasane thermal spring in Kasane was conducted with the aim of characterising it, determining the suitability of its water for drinking purposes and the influence of mineralogical composition of the rocks and precipitation on the water quality. Kasane township is situated in the Northern most part of Botswana in the Chobe District. It is a few kilometres from the Chobe River's confluence with the Zambezi River; where the four countries of Botswana, Zambia, Zimbabwe, and Namibia meet. Sixteen water samples (one from the spring, twelve groundwater samples, one river and two sewage samples), forty-nine sediment samples and three rock samples were collected to achieve this objective. The water and sediment samples were analysed for both major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), major anions (CO_3^{2-}, HCO_3^-, Cl^- , SO_4^{2-} , NO_3^-, F^-, PO_4^{3-}, NO_2^- and Br^-) and trace elements (As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn) at the geochemistry laboratories of the University of Botswana and at the Department of Water Affairs. The physico-chemical parameters such as pH, EC and TDS were measured in-situ. Petrographic analysis of the rock thin sections was also carried out to identify the mineralogical composition of the rocks of the studied area. The geology of the area is generally Karoo volcanic. Thin sections analyses revealed that the rock is basalt made up of plagioclase, clinopyroxene and opaque minerals with othopyroxene and amphibole in trace amounts. In the analysed water samples generally based on the mean values of the chemical parameters, the cations were in the order of abundance as $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Li^+$ and the anions were in the order of abundance as $Cl^- > SO_4^{2-} > HCO_3^- > PO_4^{3-} > Br^- > CO_3^{2-} > NO_3^- > F^- > NO_2^-$. In the analysed sediment samples the cations and anions are in the order of $Na^+ > Ca^{2+} > K^+ > Mg^{2+} > Li^+$ and $SO_4^{2-} > Cl^- > NO_3^- > Fl^- > Br^- > NO_2^- > PO_4^{3-}$, respectively. The spring and the groundwater from the pits north of the spring are slightly alkaline to alkaline, brackish to saline and hard to very hard whereas the groundwater west of the springs, river water and the sewage water are acidic to slightly alkaline (with the exception of sample W11, which is alkaline), fresh (with the exception of sample W12, which is brackish) and soft to hard. 75 % of the analysed groundwater samples from the pits west of the thermal spring show some similarities in the trend of concentration of the different constituents of the groundwater with the river water, suggesting that the groundwater is recent or derived from precipitation. A slight increment of values in the analysed major cations, anions, and trace elements in the groundwater of this area is due to the dissolution of different minerals in the rocks of the study area. The remaining 25 per cent the groundwater samples from this part of the study area suggest that precipitation is not the sole source of groundwater and it could be derived from both precipitation and fluids of deep origin. The thermal spring and the groundwater north of the thermal springs are characterized by higher mineralization, and this could be attributed to the more supplement of the deep fluids that have deep origin. This implies that the source of the spring and the groundwater north of the thermal spring have a regional origin. The thermal spring water and all groundwater in the studied area are not recommended for drinking purposes.

Keywords: Cations, anions, trace elements, thermal spring, hydrogeochemistry.

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LIST OF ABBREVIATIONS

BOBS ……………………..Botswana Bureau of Standards

WHO……………………….World Health Organisation

EC……………………………Electrical Conductivity

TDS………………………….Total Dissolved Solids

DWA…………………………Department of Water Affairs

ICP-MS……………………….Inductively Coupled Plasma Mass Spectrometry

HDPE…………………………High Density Polyethylene

EN…………………………….Electrical Neutrality

CHAPTER 1.0 – INTRODUCTION

1.1 Background

Water with good quality and sufficient quantity from different resources is a backbone for economic development of a country (Abreha, 2014). However, according to the Botswana Water Statistics report of 2009, Africa's water resources are threatened by the increasing population trends which result in increase in water demand by various users. In Botswana, this very precious resource is scarce due to the semi-arid climatic conditions of the country which is characterized by recurrent drought.

Hydrogeological conditions and chemical compositions of groundwater are significant constraints and limiting factors for developments such as the type of materials used for water distribution systems, the quality of constructions and local ecological values hence it is important to understand the hydrogeochemical processes and how they evolve in both ground and surface water resources (Abreha, 2014). As the chemical composition of natural water is controlled by many interrelated processes, it follows that some understanding of these processes is needed before one can speak or act intelligently toward the aim of water quality control and improvement (Hem, 1959).

In recent decades it has become evident in many countries of the world that groundwater is one of the most important natural resources. Groundwater as a natural resource is an element of the environment and it is used in human activities. As a source of water supply groundwater has a number of essential advantages when compared with surface water: as a rule it is of higher quality, better protected from possible pollution including infection, less subject to seasonal and perennial fluctuations, and much more uniformly spread over large regions than surface water.

A spring is a concentrated discharge of groundwater appearing at the ground surface as current flowing water (Todd, 1980). It may have a fairly constant or variable discharge. It may be permanent or it may be temporary. It will contain dissolved solids in the form of ions or certain dissolved gases or oils like petroleum. It may be hot or it may have a temperature that is very low.

Generally thermal springs, also referred to as hot springs, are located all over the world at special geological areas, mainly near volcanic regions. Thermal springs are by definition ‘warm’; however, there is no consensus regarding the exact temperature that distinguishes a spring from a thermal spring (Olivier et al., 2008). Two important benchmarks are recognized, namely, that of the human body (36.7˚C) and mean annual local air temperature. However, in view of the fact that the climate of one region differs from that of another, what is ‘warm’ in one region may not be considered to be such elsewhere. For this reason, the definition of a thermal spring is often based on the mean annual air temperature of the specific site (Olivier et al., 2008). LaMoreaux & Tanner (2001) define springs with a water temperature significantly (10˚F i.e. ~ 6˚C) higher than the mean annual air temperature of the surrounding area as thermal but the lack of a specific base temperature may cause difficulties in interregional comparisons.

Bow Valley Naturalists (2010) also defined thermal springs in the same way using mean annual air temperature as a base. According to them, a thermal spring is simply a point of groundwater discharge whose water temperature exceeds the regional average air temperature. According to Baioumy et al. (2014), a hot spring is a spring that is produced by the emergence of geo-thermally heated groundwater from the Earth's crust. They further state that a hot spring appears as an opening on the surface of the ground, but the source of water, source of heating, as well as possible contamination of this water, are hidden beneath the surface of the earth. Todd (1980) defined thermal springs as springs that discharge water which has a temperature above that of the normal local groundwater.

Hot groundwater and springs are associated with recently extinct volcanic fields, the deep circulation of groundwater along permeable or active faults, and heating of groundwater by slow circulation through laterally extensive aquifers at depth. According to LaMoreaux & Tanner (2001), thermal springs originate either from recent plutonic activity (volcanic origin) or from rainwater that percolates into the ground through permeable rocks or via conduits such as joints, faults and fracture zones in less permeable rocks (meteoric origin). Such water may reach considerable depths before resurfacing.

The discharge of a thermal spring is determined by the area that is contributing recharge to the aquifer, the size of the aquifer, the aquifer storage capacity, the rate of recharge, the amount of precipitation, and the transmissivity and discharge capacity of both the aquifer and the conduit through which water rises to the surface. Most thermal springs are located at topographically low points. The difference in altitude between the recharge area and the exit point determines the hydrological head, which directly affects the flow rate.

The mineral content of particular thermal water depends on where it comes from**.** Generally water in thermal spring is basic, and in some of hot springs the water is acidic (Rajapaksha et al., 2014). Chemical content of the water in thermal spring changes according to the chemical composition of rocks situated on path of the hot water flow. When the temperature of water increases, it increases the dissolving rate of minerals. Due to this, thermal springs are often enriched with trace elements. Generally, the specific chemical composition of spring water will depend largely on the composition of the rain water, its temperature and pH, and the geology of the aquifer and the rocks through which the water rises to the surface.

The socio-economic importance of thermal springs has fluctuated over time, but over the past few decades there has been an unprecedented resurgence of interest in this resource, mainly due to a diversification in the application of the waters (Olivier et al., 2011). Currently, thermal spring water is recognized for its numerous benefits. In many countries thermal springs are utilized for a variety of purposes, such as the generation of power, direct space heating, industrial processes, aquaculture, agriculture, bottled water and the extraction of rare elements (Olivier et al., 2011). Moreover, thermal water has been used for thousands of years to heal arthritis, joint pain and burns, but its primary use is to relieve the skin of certain afflictions. Thanks to its purifying effect and antioxidant properties, thermal water is the go-to product for those with a typical skin types.

Thermal springs are thus natural resources that, if developed optimally, could make a considerable contribution to the local and regional economy. However, care should be exercised when making decisions regarding the appropriate use of the springs (Olivier et al., 2008).

Like all natural resources, thermal springs should be managed in a sustainable manner. The availability of current scientific information on thermal springs and their properties is a pre-requisite for sound decision making regarding resource use and development. Unfortunately, there has not been any hydrogeochemical study of thermal springs in the Chobe District, Kasane. This research presents, for the first time, information on thermal springs located in the northern part of the country at Kasane in the Chobe District. The research focuses on the chemical composition and origin of the thermal spring waters.

1.2 Problem Statement

The Kasane thermal spring has been in existence dating from as earlier than the 1960`s but no geological mapping or hydrogeological study has been conducted and recorded about them. However, this natural phenomenon is one of a kind in Botswana and it is important to have a record of its origins as well as its physical and chemical characteristics.

The Kasane thermal spring site is used by the local community for recreation. From about the 1990`s and possibly earlier than that there has been some members of the community as well as local churches who believe that the water from the thermal springs has medicinal value and can be used to cleanse evil supernatural powers, they therefore harvest it and drink it.

Over the years developments have come in that area and the population of Kasane has grown. There are still members of the community who continue to drink this water even though they do not know its chemical composition. According to Hem (1959), the activities of man have had a major impact on the environmental factors influencing the composition of water. It can be deduced that the power of man to alter his environment is great and widely evident in the changes which he can knowingly or unknowingly bring about in the water composition. It is, therefore, important to characterize the chemical quality of this water in order to establish the health effects it may be having now or the effect it will have in future to those who drink the water and to the future generations.

This research is conducted to determine the hydro-geochemical features of the Kasane thermal springs and determine its suitability for drinking purpose. Since the optimal use of a thermal springs is largely dependent upon its physical and chemical characteristics, the results from this research can be used as a source of information in the sustainable development of this resource in the area for the benefit of the society in Kasane in particular and for the country in general.

1.3 General Objective

The main objective of this research was to determine the hydro-geochemical features of the Kasane thermal spring and the groundwater in its surrounding areas, and their suitability for drinking purpose.

1.3.1 Specific objectives

The specific objectives of the research were the following

- To determine the major cations and anions of the waters;
- To determine the trace element concentrations of the waters;
- To determine the major cations, anions and trace elements concentrations of the sediments;
- To investigate the possible and types of rock-water interaction;
- To determine the geology of the Kasane thermal spring area and their mineralogical compositions; and,
- To determine the suitability of the thermal spring water and the groundwater around it for drinking purposes.

1.4 Description of the Study Area

1.4.1 Location

The study area is situated in the northern part of Botswana at Kasane in the Chobe District. Chobe District (22, 560 km^2) is one of the smallest districts in Botswana and has an international setting. It is where Botswana meets Namibia, Zimbabwe and Zambia. Kasane is a few kilometres from the Chobe River's confluence with the Zambezi River and lies within the lines of longitude of 24^o and 26^o E, and latitude of 17^o and 19^o S (Fig 1).

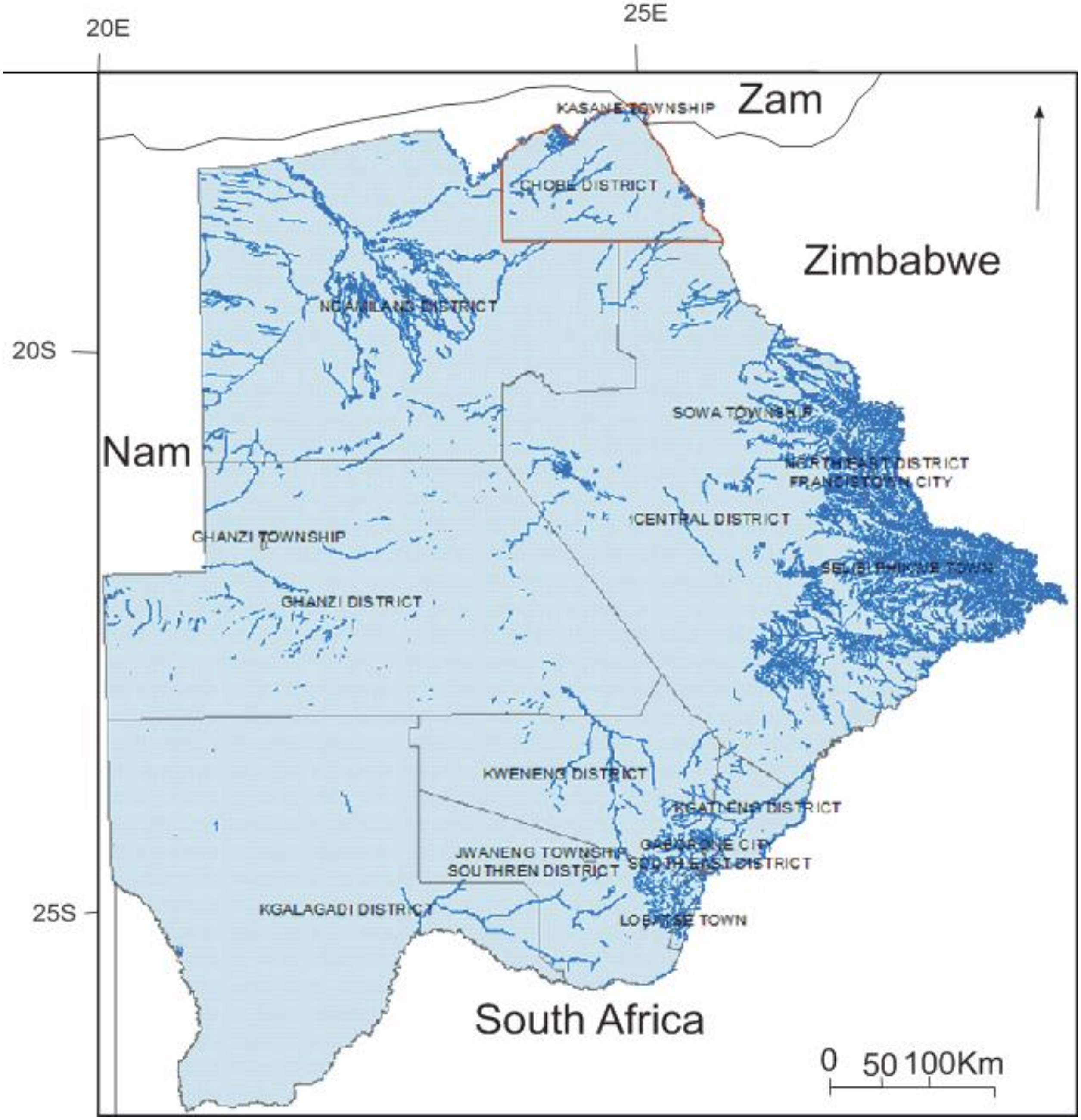


Figure 1. Location of the study area.

1.4.2 Topography and Drainage

The Chobe District in general is made up of a relatively featureless central plateau and floodplains in the north and west of the district. On the plateau, near Pandamatenga are three large flat plains.

Away from the Zambezi-Chobe floodplains is an escarpment. The floodplains are flat with several pronounced ridges. In the west is the Mababe depression, a seasonal swamp connected with the Linyanti marsh in the west through the Savuti channel.

The study area is a place situated between Kasane and Kazungula by the bank of the Chobe River. It is also almost completely surrounded by the Chobe farms fields. The Chobe River always has flowing water present throughout the year.

The whole study area drains toward the Chobe River. The Chobe River rises as the Cuando in the highlands of Angola. When it crosses into Botswana, it becomes the Linyanti, at Parakarungu it becomes the Itenge, and at Ngoma Gate it becomes the Chobe River. Finally, it joins the Zambezi at Kazungula after which they hurtle together over Victoria Falls.
The studied area consists of only one thermal spring from the alluvial sediments in the floodplain. According to the information from the elder peoples in the community, there were other thermal springs in the area. However, at present these thermal springs do not exist anymore, and nobody knows when they disappeared or where the exact positions of the springs were.

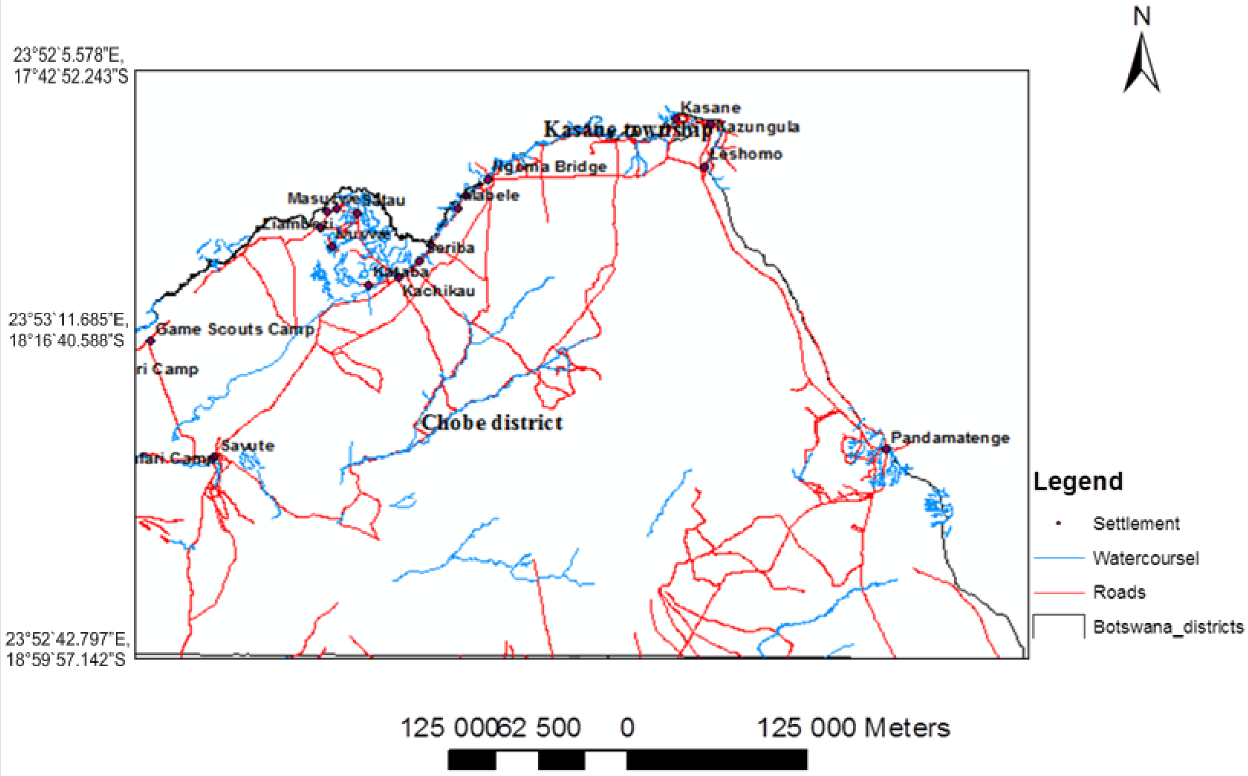


Figure 2. Chobe district.

The map above shows the Chobe district with all the villages that fall within it (Fig 2).

1.4.3 Land use

There is an acute shortage of land in the district due to the fact that about 80% of the district is devoted to conservation of the wildlife and forest resources. Human settlements account for about 20%. Land use in Chobe is determined by several factors, some of which are the increase in human population, tourism potential of the area, and governmental policies. Particularly in Kasane, the dominant land uses are grasslands, croplands and floodplains (swampy area). The area within 40 km of this station is covered by grasslands, croplands, and floodplains. The local people harvest water from the spring (Fig. 3).

Figure 3. The only thermal spring which is visible (Locals place logs around it so that they can fetch the warm water in bottles).

1.4.4 Soil

The soils of the Chobe district can be divided into sandy soils in the centre, deep clay on the plains of Pandamatenga, and loamy clay and sand along the Chobe River and in the Enclave. Soil in Kasane is dark clay in the flat land and is comparatively fertile for arable agriculture whereas on other patches and along the Chobe River it is sand.

The soil at the study area is dark clay and sandy soil at some areas towards the river bank.

1.4.5 Vegetation

Along the Chobe river-front there is a narrow stretch of riverine forest. Teak forests occupy parts of the district with sandy soils and the dominant species are the Zimbabwean teak (*mukusi*) and bloodwood (*mukwa*). The Mababe depression is occupied by acacia and *mophane*, with some portions occupied by open grassland. The western part of the district is occupied by a mosaic of tree and shrub savannah with *mophane* as the dominant species while the floodplains of the Linyanti-Chobe river support aquatic grassland vegetation with islands of *mokola* palm. The large plains of the Pandamatenga are open grassland. There is limited availability of good grass species for livestock grazing. The area understudy, particularly, is characterised by grass even though the area surrounding it has trees (Fig 4).

Figure 4. Grass that dominates the vegetation around the study area.

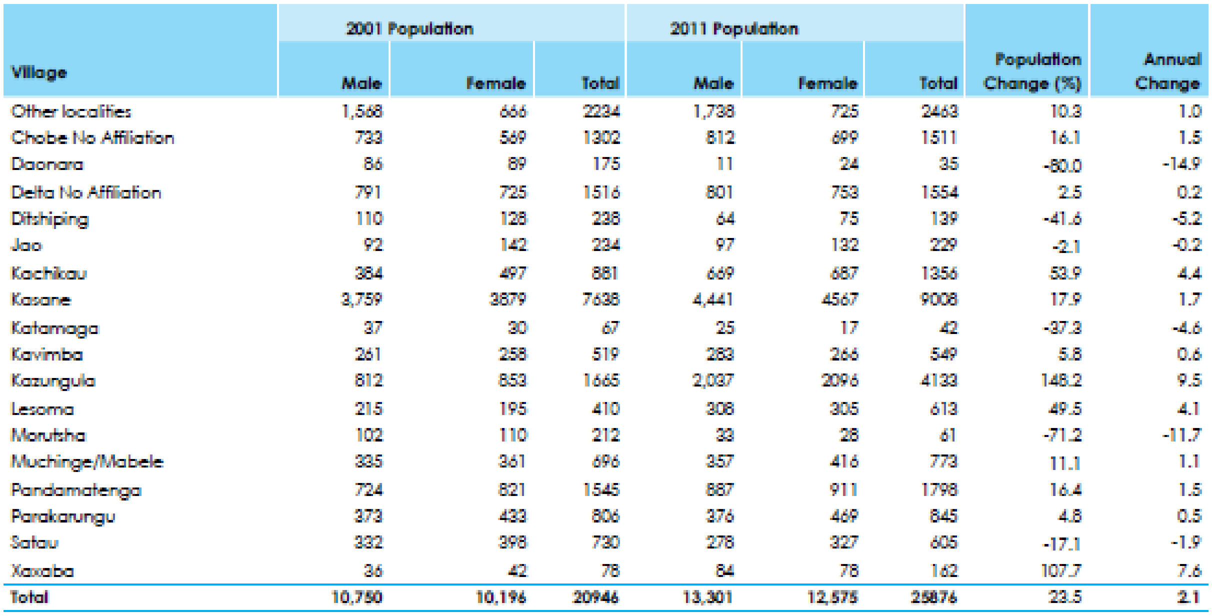
1.4.6 Climate

The climate in Kasane is referred to as a local steppe climate or a hot semi-arid steppe climate. During the year, there is little rainfall in Kasane. In a year, the average rainfall is 643 mm. Generally, the annual rainfall varies between 550 mm and 650 mm being the highest in the country and the least variable. The least amount of rainfall occurs in July. The average in this month is 0 mm. Most precipitation falls in January, with an average of 158 mm. The variation in the precipitation between the driest and wettest months is 158 mm.

Over the course of a year, the temperature typically varies from 9°C to 35°C and is rarely below 6°C or above 37°C. The warm season lasts from September to November with an average daily high temperature above 33°C. The cold season lasts from June to August with an average daily high temperature below 27°C.

1.4.7 Population

The villages that are closest to the study area in the Chobe District are Kasane and Kazungula. According to the report of population and housing census done in 2011 by the Central Statistics Office of Botswana, the population of Kasane has grown by 17.9% from 2001 to 2011, from a total of 7638 in 2001 to 9008 in 2011 whereas the population of Kazungula has had a change of 148.2% from a total of 1665 in the year 2001 to 4133 in the year 2011. This is shown in figure 5 below.



Village	2001 Population			2011 Population			Population Change (%)	Annual Change
	Male	Female	Total	Male	Female	Total		
Other localities	1,568	666	2234	1,738	725	2463	10.3	1.0
Chobe No Affiliation	733	569	1302	812	699	1511	16.1	1.5
Daonara	86	89	175	11	24	35	-80.0	-14.9
Delta No Affliation	791	725	1516	801	753	1554	2.5	0.2
Ditshiping	110	128	238	64	75	139	-41.6	-5.2
Jao	92	142	234	97	132	229	-2.1	-0.2
Kachikau	384	497	881	669	687	1356	53.9	4.4
Kasane	3,759	3879	7638	4,441	4567	9008	17.9	1.7
Katamaga	37	30	67	25	17	42	-37.3	-4.6
Kavimba	261	258	519	283	266	549	5.8	0.6
Kazungula	812	853	1665	2,037	2096	4133	148.2	9.5
Lesoma	215	195	410	308	305	613	49.5	4.1
Morutsha	102	110	212	33	28	61	-71.2	-11.7
Muchinge/Mabele	335	361	696	357	416	773	11.1	1.1
Pandamatenga	724	821	1545	887	911	1798	16.4	1.5
Parakarungu	373	433	806	376	469	845	4.8	0.5
Satau	332	398	730	278	327	605	-17.1	-1.9
Xaxaba	36	42	78	84	78	162	107.7	7.6
Total	**10,750**	**10,196**	**20946**	**13,301**	**12,575**	**25876**	**23.5**	**2.1**

Figure 5. The population of the Chobe district in 2001 and 2011.

1.5 Geology of the study area

1.5.1 Regional geology

The main geological units of northern Botswana are presented in Figure 6 below. The boundaries between the main lithostratigraphical units are commonly not exposed but were inferred using aeromagnetic data (Kampuzu et al., 1998). The area is predominantly underlain by the Kalahari Copper Belt which extends from Namibia to North-west Botswana for about 800 kilometers (Maiden & Borg, 2011). In North-west Botswana the copper-belt is known as Ghanzi-Chobe Belt and it is poorly exposed due to sand cover. The belt comprises of volcano-sedimentary rocks and are exposed on the widespread sands of the Kalahari Desert, Western-North Botswana. The volcanic component is Neoproterozoic and much older than the sedimentary component which is pan-African (Kampunzu et al., 1998). The volcanics represent a bimodal suite that consists mainly of rhyolite and subordinate basalt constituting the Kgwebe Formation. The Kgwebe Formation overlies the Paleoproterozoic basement comprised of granitods and various metamorphic rocks (Fig. 6).

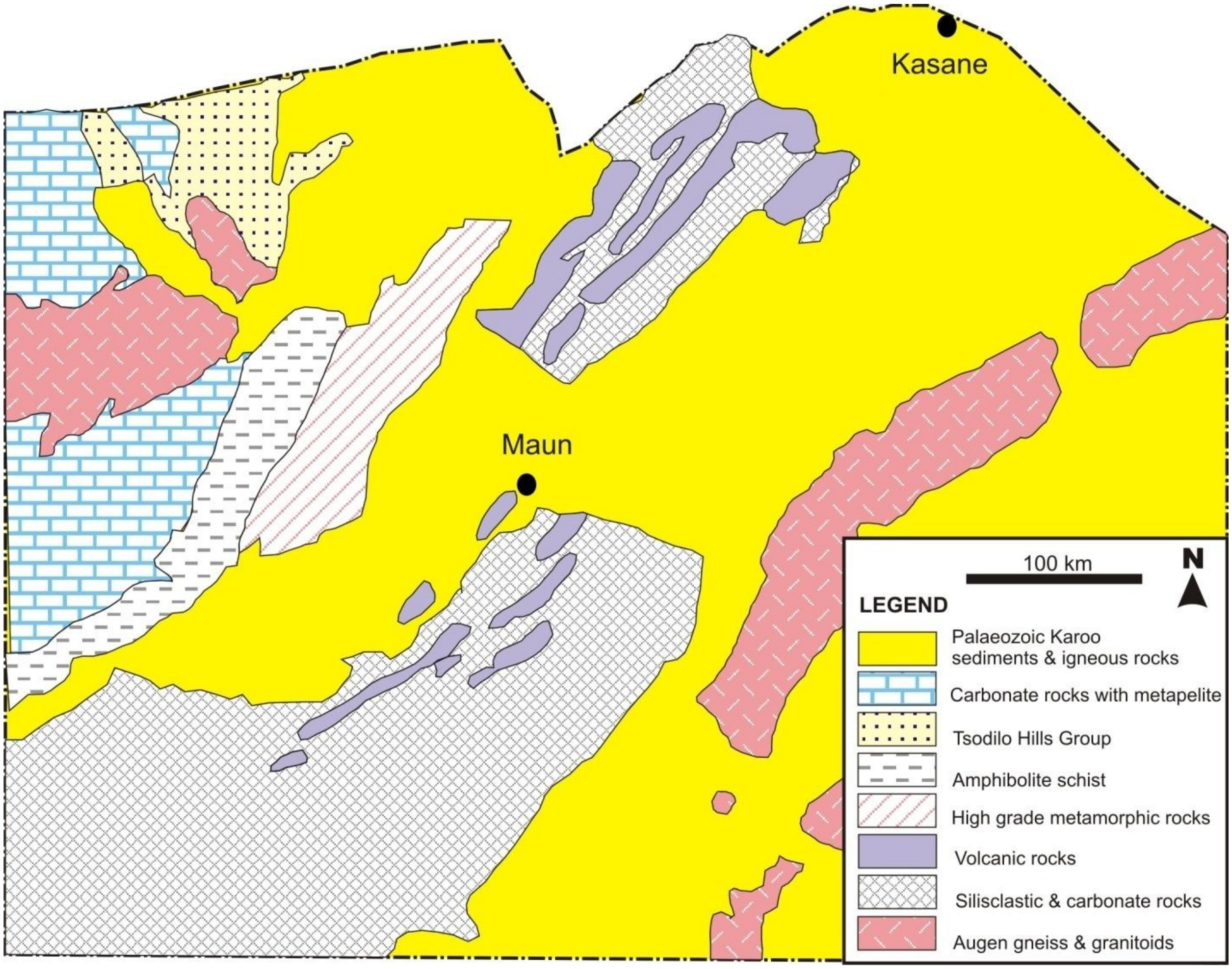


Figure 6. Regional geological map of north-west Botswana (modified from Kampunzu et al., 2000).

The basement and volcanics are uncomformably overlain by the siliclastic and carbonate rocks of the Ghanzi, Tsodilo and Xaudaum Groups (Modie, 2000; Wendorff, 2005). The Ghanzi Group, which overlies the volcanics is divided into three main formations namely Ngwako pan, D'kar and Mamuno Formations. The Ngwako pan Formation, which is the basal part of the Ghanzi Group, consists of grey matrix rich sandstone followed by conglomerate and reddish mudstone. Overlying the Ngwako pan Formation is D'kar Formation which consists of copper-sulphide mineralization at the base, and dominated by green grey sandstone-siltstone with subordinate oolitic limestone. The Mamuno Formation, which is the top formation, is characterized by reddish sandstone, siltstone and mudstone with subordinate limestone (Modie, 2000). A summary table of the stratigraphy of the Ghanzi Group is presented in Figure 7.

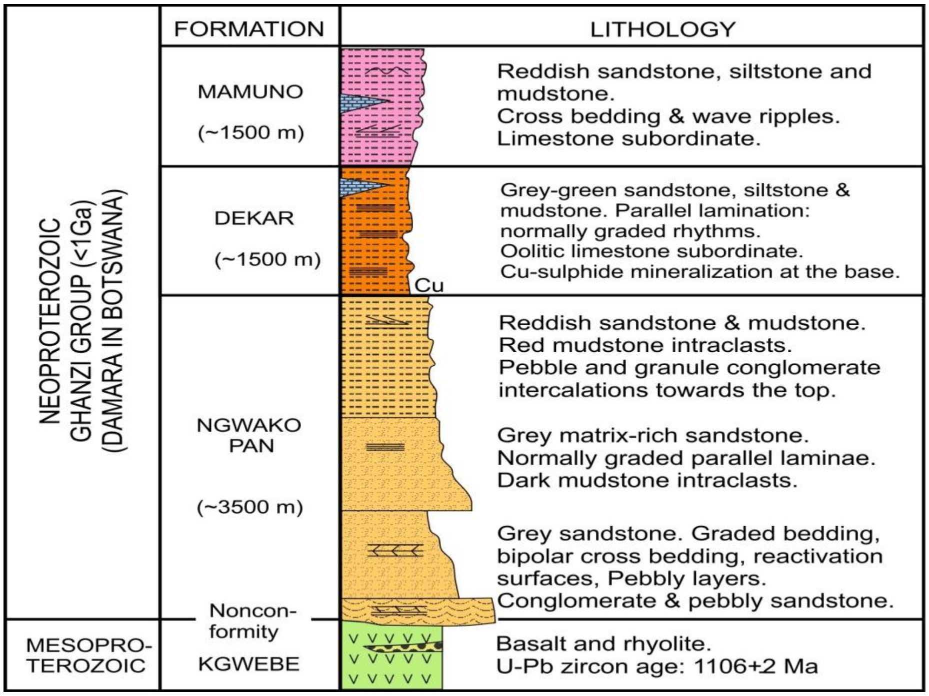


Figure 7. Lithostratigraphy of the Ghanzi Group in Botswana (from Kampunzu et al., 1998).

The Tsodilo Hills Group is an association of ferruginous and micaceous quartzite, quartz–mica schist, metamorphosed conglomerate, minor shale, phyllite, sandstone and ironstone, which have been altered to kyanite metamorphic grade (Singletary et al., 2003). Shallowing-upwards sequences of varying thickness, with or without conglomerates are characteristic of the Tsodilo Hills succession (Wendorff, 2005). Pebbly deposits usually occur as topmost components of sequences coarsening upwards from quartzite to pebbly quartzite to conglomerate. According to Wendorff (2005) the lithological development of the Tsodilo Hills Group suggests that the deposition took place on a marine shelf supplied with mature siliciclastic material and influenced by tidal and littoral long shore currents.

The Xaudum Group is composed of low-grade meta-sandstone, meta-siltstone and carbonate rocks with cherts (Key & Ayers, 2000). The Xaudum Group rocks are younger than 1.02 Ga (Mapeo et al., 2000). These Precambrian rocks are largely concealed beneath the Carboniferous to Jurassic Karoo Supergroup and Cenozoic Kalahari Group sedimentary rocks.

1.5.2 Local geology

The local geology is comprised of the Karoo Supergroup rocks as can be seen in Figure 8. The Kalahari Basin is amongst the several contemporaneous basins in southern Africa which covers an extensive area in Botswana (Fig.8). The Kalahari basin is contiguous to the Mid-Zambezi basin which is located in the northwestern part of Zimbabwe. The boundary between the two basins is not well defined. The top most geologic unit in the Kalahari Basin is the basalt of the Stormberg Lava Group (Johnson et al., 1996). Based on the stratigraphic section obtained in the eastern part of the Kalahari basin, the Stormberg Lava Group is underlain by the sandstone of Ntane Formation which in turn overly the Mosolotsane Formation which is essential made up of arenaceous sediments of fluvial origin. Below the Mosolotsane Formation is the Tlhabala Formation which conformably overlies the Tlapana Formation. The Tlapana Formation is comprised of mudstones, carbonaceous shales and coal seams. It overlies the Mea arkose Formation which is generally composed of pebbly sandstones and conglomerates (Modie & Le Herisse, 2009).

The adjacent Mid-Zambezi basin contains a thick basaltic rock at the top which belong to the Batoka Formation. The basalt is underlain by the Forest Sandstone Formation comparable to the Ntane Formation. Below the Forest Sandstone occurs the pebbly arkose and fine red marly sandstone with ripple marked flagstone at the bottom. This unit is a correlative of the Mosolotsane Formation (Johnson et al., 1996). It is important to note that the study area (Kasane) is located mid-way between the Kalahari and Mid-Zambezi basins (see Fig.8). Though the area is considered to be part of the Kalahari basin, there is no lithostratigraphic data from the area to confirm the stratigraphic column of the Karoo sequence in the area since there are no boreholes drilled in the area or in the vicinity of the area in Botswana.

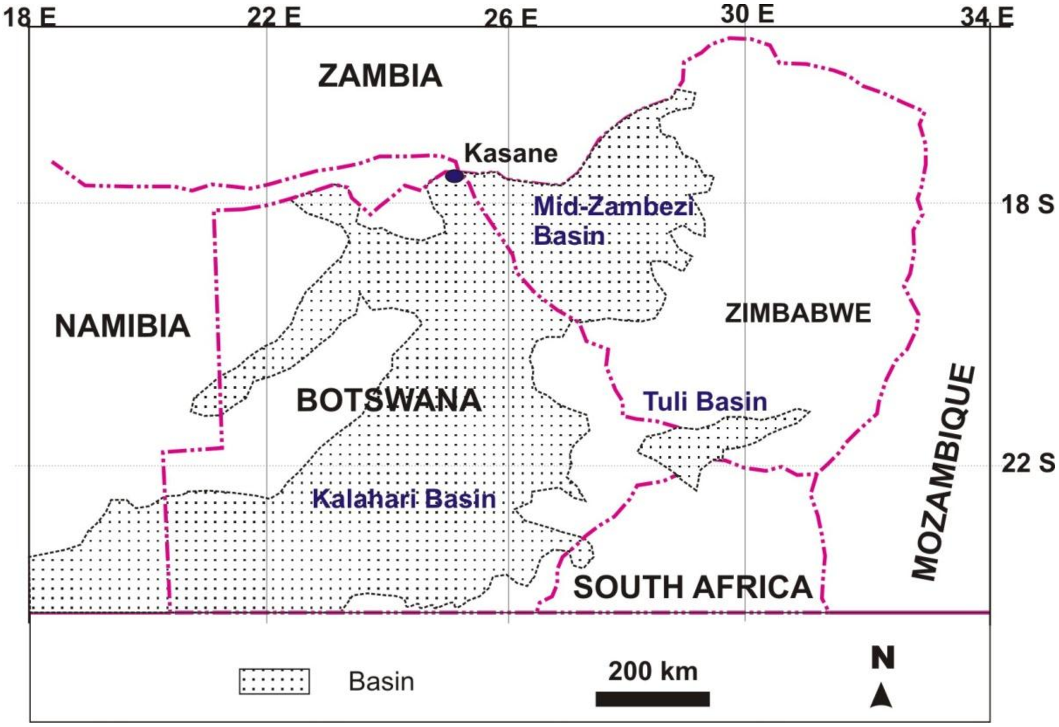


Figure 8. Map showing the Karoo basins in the study area (modified from Johnson et al., 1996).

CHAPTER 2.0 - LITERATURE REVIEW

2.1 Parameters of water quality

Abreha (2014), in his study on the hydrogeochemical and water quality investigation on irrigation and drinking water supplies in the Mekelle region, Northern Ethiopia, indicated that in the determination of the chemical composition of the groundwater the following processes should be taken into consideration; water-rock interaction, recharge and discharge, atmospheric inputs, inputs of chemicals by human activities, geological structure, mineralogy of aquifers and the geological processes within an aquifer. The author stated that these different processes will lead to various water types and also give an idea of the geological history of the enclosing rocks. Abreha (2014) further listed the following as some of the water parameters that should be considered when carrying out a hydrogeochemical analysis; temperature, conductivity, alkalinity, dissolved oxygen, pH, cations and anions, hardness, TDS, sodium adsorption ratio and saturation index.

In addition Kreye et al. (1996) said a common minimum field analysis should include: TDS (or specific conductance), temperature, pH and Nitrate-nitrogen and that site investigation should verify site conditions, gather additional data to further characterize the springs and source area, identify local scale features, and survey the waterworks.

2.2 Characteristics of springs

Bryan (1919) stated an essential point in a study done on the classification of springs that springs may be divided according to temperature into thermal and non-thermal springs. Most non-thermal springs have temperatures that are approximately the same as the mean annual temperature of the air of the region in which they are found. The division between thermal and non-thermal waters is usually fixed at 70° F., but 20° to 25° above the mean for the region might be preferable. Thermal springs are usually called "hot," but those of slightly lower temperature are sometimes called "warm." Cold springs have temperatures below normal. Also, boiling springs have a sandy bottom, through which the water emerges with some force. The sand is constantly agitated and appears to boil. Bubbling springs, also called boiling springs, are due to the emission of gas or vapor with the water. Certain hot springs actually boil in the ordinary sense. Usually emission of air or gases gives the impression of ebullition. Carbonated springs, which emit carbon dioxide, are the most common bubbling springs. Nitrogen, hydrogen sulphide, sulphur dioxide, marsh gas, and other gases have been found in spring waters. Bubbling is also produced by the emergence of water from a well-defined opening under considerable pressure into a pool of water. The surface of the water is domed, and slight fluctuations in volume or pressure give a bubbling effect.

In addition, the author stated that springs may also be divided according to perennial or permanent springs flow throughout the year. Intermittent or temporary springs flow only during or after rain. Where evaporation is high the flow of springs is much decreased or may cease during the warm season. Some springs flow only at night because of a very delicate adjustment between supply of water and evaporation.

2.3 Chemical characteristics of hot springs

Subtavewung et al. (2005) carried out a study of the characterization and classification of the hot springs in Thailand. The criteria they used for characterizing and classification of the hot springs in Thailand are surface temperature, conductivity, alkalinity, acidity, TDS, pH values, H_2S, Ca, Cl, F, Fe, K, Mg, Mn, Na, NH_3, SiO_2 and SO_4 contents.

Accordingly, the one hundred and nine data of hot springs in Thailand indicated that 41 hot springs (37%) are thermal springs whereas 68 hot springs (63%) are hyperthermal springs. Twenty-four percent of hot springs show neutral (pH = 6–7.5).

Olivier et al. (2011) carried out a study at the northern part of the Limpopo Province, South Africa and their main objective was to establish the thermal and chemical characteristics of hot water springs. Their study area was comprised of the following hot springs; Evangelina, Tshipise, Sagole, Môreson, Siloam, Mphephu, Minwamadi and Die Eiland. Field data and water samples were collected from the hot springs mentioned above. The geology of the study area was explained to include various lithologies of the Soutpansberg Group and Karoo Supergroup, as well as the Goudplaats-Hout River Gneiss Suite and the Beit Bridge Complex. They collected the water samples from the 8 thermal springs and stored them at low temperatures of around 4°C in 1-litre sample bottles before being submitted to the Institute for Soil, Climate and Water at the Agricultural Research Council in Pretoria for chemical analysis. They classified the springs in the northern part of Limpopo as scalding (58°C and 67.5°C), hot (42°C - 45°C), and warm (29°C - 34°C). From their findings they presented that water samples from the northern Limpopo springs share a number of chemical characteristics. They stated that springs have a pH of around 8; they are neutral, that is, neither corrosive nor depositional: pHs – pH = -1 to +1. Mphephu, Minwamadi, Siloam, Tshipise and Sagole were found to have temporary hard carbonate waters while

Evangelina and Die Eiland had highly mineralized chloride-sulphate waters. Die Eiland and Tshipise were classified as saline waters (936 to 2364 mg/l TDI). Using the same criterion, Evangelina's water was also classified as saline. In terms of major ions, only water from Minwamadi and Sagole was identified as suitable for human consumption – the other springs having fluoride values exceeding the recommended South African Guidelines for Domestic Water Quality (DWAF, 1996) value of 1 mg/l.

Merkel (2006) carried out a preliminary hydrogeological investigation on the Nhambita hot spring, Mozambique. The goal of the study was to investigate the hot spring with respect to the origin of the water, the discharge, its chemical composition and to determine the suitability of the Nhambita hot spring for tourism development. The author used the Koppen climate classification system and classified the climate of central Mozambique as tropical savannah. The area of investigation is situated close to the East African rift (EAR) zone and is characterized by the association of Tertiary to recent volcanism and anomalous topographic swells. The Nhambita hot spring is sitting more or less on the triple junction of a fault systems thus the amount of groundwater available is limited.

During field investigations four water samples were taken for laboratory investigation. The EC was found to be 1680 µS/cm with the total dissolved solids (TDS) of 989 mg/l. Merkel (2006) mentioned that in some countries mineral water is defined by the criteria TDS > 1 g/l. In terms of this criterion the Nhambita water would miss it by a few milligrams. The Nhambita spring water has a discharge temperature of 62°C and is therefore thermal water according to Mozambique standards. If the water is tapped by a drilled well, the temperature will be even higher than 62°C, but the excess heat can be used as alternative energy. Sediment temperature of 67°C in 15 cm depths observed was an indication for higher temperature with depth.

From the ratios Br/Cl and I/Cl which are both 2.5×10^{-3} in the Nhambita hot spring it was excluded that the chloride has its origin in seawater, since seawater has a Br/Cl ratio of 3.5×10^{-3} and an I/Cl ratios of 0.0027×10^{-3}. Thus, all three halogens stem from water dissolving silicate rocks which is an agreement with investigations of silicate rocks in Namibia where comparable rations for both Br/Cl and I/Cl were obtained. The I/Cl ratio indicates silicate rocks as origin for the elevated chloride concentrations which supports very long mean residence times. Therefore it is very unlikely that the water contains man made contaminants e.g. pesticides.

According to Merkel (2006) one or two other geothermal springs has existed but the knowledge about the exact position is lost or these one or two springs do not exist anymore. Two possible reasons stated by the author were that there was a natural self-sealing process due to precipitation of minerals that consequently decreased the permeability for the upwelling groundwater or man made over pumping of an aquifer. The water is characterized by the major ions sodium, sulfate and chloride with elevated concentrations of fluoride, phosphate, and nickel. The elevated sulfate concentrations might have slightly laxative effects, which might be used to cure constipation. Considerably low are the concentrations of calcium, magnesium and total dissolved inorganic carbon (TIC) while fluoride and phosphate are elevated. The low TIC (total dissolved inorganic carbon: HCO_3^-, CO_2, CO_3^{2-}) is a clear indication that the water was not in contact with a still active volcanism. The high phosphate concentrations are probably one reason for the algae growth in the flow channel and one can observe a rapid decrease of phosphate in the flow channel.

The water is low in natural toxic elements like arsenic, lead, cadmium, mercury, beryllium, selenium, antimony, and uranium. Merkel (2006) stated that although there is no evidence that the chemical composition of the water is changing very much by time, the water should not be used as regular drinking water since the fluoride and nickel concentrations exceed international limits. However, there is no concern to use the water as bottled mineral water or medicinal water, since the water does not contain any pathogen bacteria. It contains no tritium and is therefore “older” than 40 years, contains no significant young components, it is about eleven thousands years. This is in agreement with the fact that the water contains no pathogenic micro-organisms, it is also in accordance with low dissolved organic components (DOC, 0.3 mg/L). According to the δ14C concentration of 24.47 ± 0.14 the corrected mean residence time in the subsurface of the Nhambita hot spring water is 11.310 ± 45 years.

The water in the associated stream is very similar to the water of the Nhambita hot spring. One can therefore assume that the diffusive discharging water has the same composition and the same source. Attempts were made to protect the hot spring by a dam against inundation from upstream, but it can be speculated that this dam was not able to protect the hot spring against inundation due to back flow of flood water. There is some evidence that the use of agro-chemical is restricted at the very moment to growing of cotton. Household rubble is very scarce and is buried in private owned pits. Open area fecation is widely used and is probably the most concerning item during a flood flow.

Wen et al. (2013) carried out a study on the arsenic, fluoride and iodine in groundwater of China and they mentioned hydrogeologic and hydrogeochemical conditions favouring high arsenic in groundwater. They stated that for arid and semi-arid inland basins of north China, high arsenic groundwater occur frequently in aquifers with organic-rich fluvial–lacustrine deposits, where the flat, low-lying topography leads to long residence time of groundwater that evolves to be weakly alkaline and frequently strongly reducing.

They mentioned two known hydrogeological conditions that favour accumulation of aqueous arsenic that is mobilized from aquifer sediment. The first being, the aquifer consisting of sediment, which is typically geologically young and the syndepositional arsenic has not been flushed out. Second, if groundwater has a long residence time as a result of sluggish flow in flat areas such as deltas or flood plains.

In their investigations they also identified that weakly alkaline to alkaline pH conditions were common for the high arsenic groundwater in inland basins of north China, suggesting enhanced mobility of arsenic because adsorption of arsenic to the iron minerals that are carrier phases is poor under alkaline pH conditions. Bicarbonate (HCO_3) was found to be typically the most abundant anion, with some waters being chlorine (Cl) dominant. In all the basins, groundwater's evolved from calcium (Ca)-dominant to sodium (Na)-dominant and sometimes Cl-rich when evaporation plays a role in the low lying parts of the basins.
In the guide basin they mentioned that the presence of arsenic was attributed to geothermal origins.

Rowe et al. (1973) carried out a study on the chemical analysis of thermal waters in Yellowstone national park, Wyoming. The authors did analyses of results for 166 samples collected during 1960-65 from 89 geysers, pools, and hot springs then compiled together with previous analyses to provide a comprehensive collection of available analytical data on the thermal waters of Yellowstone National Park, Wyo. Most of the samples were collected in polyethylene bottles, but samples for the determination of HCO_3^- and CO_3^{2-} were collected in glass bottles. The collected data were pH, temperature, silica, aluminium, iron, calcium, magnesium, sodium, potassium, lithium, ammonia, bicarbonate, carbonate, sulphate, chloride, fluoride, boron, arsenic, and the semi-quantitative spectrographic analysis of residues from evaporation of some of the waters. Temperature measurements were made either by a portable potentiometer and a copper-constantan thermocouple passing through the aluminium tube and lowered into the hot spring with the aid of a lead weight, or by a maximum thermometer suspended from the end of the rod. Field pH measurements were made with a portable pH meter using a high-temperature glass electrode.

The authors stated that the springs at Mammoth issue from Mesozoic shales and sandstones and the limestone is present deep in the stratigraphic section. They went on to state that springs at Norris Geyser Basin and those between Norris Geyser Basin and Lower Geyser Basin issue from Cenozoic rhyolitic ash-flow tuff. All the other springs listed which were part of the analysis were said to be within a large caldera and issue from Pleistocene rhyolite or glacial sediments derived mainly from rhyolite.

The hot springs of Mammoth were noted to have waters that were particularly rich in bicarbonate, sulphate, calcium, and magnesium. They stated that the chloride content was relatively low and sodium was present in excess of chloride. They further stated that the silica content was very low and the potassium content, relative to sodium, was very high. The composition of the hot-spring water was said to reflect reaction with carbonate sediments at depth.

At Norris Geyser Basin, they distinguished two types of chloride-rich hot spring waters by their potassium-lithium and potassium-sodium ratios. They found that both ratios were generally lower in waters from the western part of the basin than in waters of the eastern part. In other respects, they found that the chloride-rich waters at Norris Geyser Basin were very similar: They had the highest silica and chloride contents and the lowest bicarbonate contents of any waters in Yellowstone. The very low bicarbonate content left the pH of the water essentially not buffered so that mixing with a very small amount of acid sulphate water could lower the pH to 3 or 4.

They stated that little silica occurred because although silica deposits readily from the neutral waters, dissolved silica polymerizes very slowly in the acid chloride water. Acid sulphate waters were found throughout Yellowstone, particularly at higher elevations and at the Mud Volcano area.

The acid sulphate waters were said to may have formed when steam, rich in acid-forming gases, intersects near-surface groundwater. The concentrations of sodium and potassium were low in this type of water, but the potassium-sodium ratio is very high. These waters were relatively rich in aluminium and iron and poor in chloride. Compared with the chloride-rich alkaline waters of the Norris Geyser Basin, neutral to alkaline hot-spring waters within the confines of the caldera contain comparatively low concentrations of chloride, potassium, silica, and boron and high concentrations of fluoride, bicarbonate, and carbonate.

Jonker et al. (2013) carried out a study on the association between physical and geochemical characteristics of thermal springs and algal diversity in Limpopo province, South Africa; this was also the main aim of the study. To achieve this objective, an analysis of the algae found was carried out under microscopes and a chemical analysis of the water from the thermal spring was also done.

They carried out an analysis from 6 thermal springs located in 2 regions in the vicinity of the Soutpansberg, in the northern part of the Limpopo Province. Tshipise, Sagole, Siloam and Mphephu are found in the Soutpansberg Mountains, while Eiland and Soutini are located to the east of the Drakensberg, in the Limpopo lowveld. The source water temperatures were measured as close as possible to the eye of the springs using a temperature probe. The pH and electrical conductivity (EC) were measured in the field by Wissenschaftlich Technische Werkstatten electrodes. Measurements were replicated thrice.

Water samples collected from Mphephu, Siloam, Tshipise, Sagole and Eiland in August 2010 were analysed at an accredited laboratory. All samples were analysed for trace minerals, including copper, cobalt, zinc, manganese, boron and molybdenum, elements known to be essential micronutrients for blue-green bacteria. All chemical analyses were carried out by the ARC-ISCW using inductively coupled plasma – atomic emission spectroscopy (ICP–AES). Analyses were conducted on 31 micro-elements. Source water temperatures at the thermal springs in the study area range from 40°C to 67.5°C. Waters of most of the thermal springs in the study area was found to be alkaline (pH >8), with the exception of Eiland and Soutini which have pH values in the neutral zone. Sodium, potassium, magnesium and calcium, as well as nitrates, phosphates and sulphates, were present in very low concentrations in all springs, except for Eiland and Soutini. High sulphate levels were measured at Eiland (143.63 mg/l) and Soutini (759 mg/l), while maximum sulphate concentration recorded at most other springs were 53 mg/l or less. Nitrate concentrations were negligible, except at Eiland, Soutini and Mphephu. Phosphates were absent or present at very low concentrations in the source waters of all springs, with the exception of Eiland. The concentration of trace elements at the springs shows that the concentrations of boron were low (< 60 μg/l) at Sagole, Siloam and Mphephu, but much higher (more than 200 μg/l) at Tshipise and Eiland. Nickel levels were also high at Tshipise. Most of the other trace elements were considerably higher at Eiland and Soutini, mirroring the pattern of the macro-element concentrations. The trace elements necessary for algal growth, namely, copper, molybdenum, manganese, cobalt and vanadium, were found at relatively low concentrations (or may even be absent) in many of the springs – the exceptions being Eiland and Soutini.

Liu et al. (2011) carried out a study on the characteristics and origins of hot springs in the Tatun Volcano Group in Northern Taiwan. The aim of the research was to study the origins and processes in volcanic gassing and reservoir in different types of hot springs for geochemical investigations in the geothermal areas of the Tatun volcano group. The authors collected samples and filtered them through 0.45-μm cellulose filters in the field and stored in high-density polyethylene bottles. For cations analysis, they added ultra-pure HNO_3 after filtering to prevent precipitation in the field. In the laboratory, Yt-trium was added in the samples as the internal standard. They measured the anions and cations using an ion chromatograph (IC, Type Met-Rohm) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Type Jobin-Yvon ULTIMA2), respectively. The samples were also acidified and then the dissolved sulfate is precipitated by adding $BaCl_2$, as barium sulfate ($BaSO_4$).

Their result indicate the major cations of all thermal water in the TVG were Na+, K+, Mg^{2+} and Ca^{2+} , having a concentrations ranging from 5.5 to 1496 mg/l, 1.5 to 253 mg/l, 2.0 to 209 mg/l, and 5.3 to 382 mg/l, respectively. The major anions that were found in all samples in the TVG are SO_4^{2-}, HCO_3^- and Cl^- with concentrations ranging from 113 to 9980 mg/l, 56.3 to 777 mg/l, and 9.2 to 3990 mg/l, respectively.

According to host rocks, pH values, and major elements, the hot springs from TVG were classified into 3 types; SO_4^{2-} acidic thermal water, Cl^- acidic thermal water and HCO_3^- near neutral hot spring (Liu et al., 2011).

The SO_4^{2-} acidic thermal water, named Type I, was characterized by the occurrence of yellowish dendritic sulfur crystals precipitated around the rims of fumaroles and by strong degassing of volcanic gases. This thermal water was said to be predominantly distributed around volcanic centers with host rocks consisting of andesitic breccias and/or lava flows. In situ measurements of temperature, TDS, and pH were conducted and the values ranged from 42.8°C to 93.0°C, 245 to 12900 mg/l, and 1.5 to 3.2, respectively.

The HCO_3^- near neutral hot spring (Type II) was described as thermal water that was predominantly distributed in host rocks of fresh or less altered andesitic breccias and/or lava flows with weak degassing of volcanic gasses. In situ measurements of pH, temperature and TDS ranged from 5.8 to 6.5, 40.6°C to 61.7°C, and 295 to 1149 mg/l, respectively.

The Cl^- rich acidic thermal water (Type III) was characterized by chloride rich and low pH values. Field measurements showed that the pH values were between 1.2 and 1.9. Moreover, temperature and TDS of this type ranged from 71.8°C to 90.8°C and from 17400 to 19800 mg/l, respectively.

In general, they summarized the source of thermal water or hot spring as follows: that meteoric water circulates to depth, is heated by magma or the normal geothermal gradient, then reacts with minerals or host rocks, magmatic fluids, formation water or seawater that may have changed composition in the reservoir, and is finally driven to the surface by thermal convection. They stated the possible source components involved in producing thermal water or hot spring. These included meteoric water, seawater/formation water, magmatic fluids, host rocks and clay minerals.

Soulsby et al. (1999) carried out a study on the hydrogeochemistry of montane springs and their influence on streams in the Cairngorm Mountains, Scotland. Their main aim was to make a detailed examination of the hydrological and hydrochemical processes influencing shallow springs in the Allt a' Mharcaidh catchment in the Cairngorms. Spring water was collected at fortnightly intervals from a spring which was observed to be perennial.

The authors stated that they could not measure the flow at the site continuously because of the remoteness of the spring as well as resource constraints. They sampled water at a tributary which was approximately 1.5 km downstream as the spring formed the source of one of the major tributaries of the Allt `a Mharcaidh. Other additional data which they collected was the precipitation at 4 sites around the catchment in the form of rainfall and snow. Rainfall was collected throughout the year whereas snow samples were collected during the winter months. They conducted an analysis for pH, alkalinity and major cations and anions as well as having the oxygen isotope ratio of $^{18}O/^{16}O$ measured on all the samples they collected. For modeling the major hydrogeochemical reactions contributing to the evolution of spring water chemistry over the year they used a computer code called NETPATH.

The results of the chemical analyses showed that the ionic concentrations in both spring water and precipitation were derived mainly from marine sources. The dominant cation was sodium and the dominant anion was chloride. The authors stated that the explanation to why the ionic concentrations in the spring water were low was that the circulation of groundwater was shallow. When comparing the elements found in the spring water and from precipitation, they found out that the spring water was more enriched in most elements.

The mean pH of the spring water measured was 5.87 whereas the pH of the precipitation was 4.88. In terms of the alkalinity they found out that even though there was enrichment of weathering derived elements such as Si, Na, Mg, Fe and Al, the concentrations were very low and the alkalinity generated was extremely limited to18 µeq/l. The chloride concentrations of the spring water and of the precipitation were found to be equal. The authors described this as an indication of low evaporation rates and high altitudes where soils are freely draining and with short patchy vegetation cover therefore minimizing transpiration rates. SO_4 enrichment in spring water probably reflects enhanced inputs in occult and dry deposition at high altitudes, particularly on winter snowpack surfaces.

Concentrations of N, both NO_3-N and NH_4-N are very low in spring water and below detection for much of the year. It does appear however that, some atmospheric N is retained within the vegetation and soils of the spring catchment.

2.4 Chemistry of hot springs related to geology

Homma & Tsukahara (2008) carried out a study at the Otari and Hakuba villages investigating the chemical characteristics of hot spring water and geological environment in the northernmost area of the Itoigawa Shizuoka tectonic line. The area is, however, divided into two areas by the Itoigawa Shizuoka Tectonic Line (ISTL) which are the Hida Gaien belt area and the Fossa Magna area. Their aim was to find a relation between the geological structure and chemical composition of the hot spring water. They also analysed river water near the hot spring for comparison with hot spring water. They used the Ion chromatograph for major ion components such as Na^+, K^+, Ca^{2+},

Mg^{2+}, Cl^- and SO_4^{2-}. They then used the ion balance calculation to establish the HCO_3^-. They found out that the major cations of Na^+, K^+, Ca^{2+} and Mg^{2+} generally originated from the mother rocks of the hot spring. They furthermore found out that the concentrations of ions in hot spring water were all higher than in the river water except for SO_4^{2-} in the Fossa Magna area. They concluded that the source material for the SO_4^{2-} in the river water was pyrite. However, the concentrations of ions in the Hida Gaien belt area were higher in the hot spring compared to the river water which was what they expected. The other findings was that the water from the hot springs contained a high concentration of Mg^{2+} and that the ratio of Mg^{2+} to total cations was extremely high, they explained this to be due to the formations around the reservoir, the ultramafic rocks such as serpentinite.

Bryan (1919) explained that temperature, dissolved salts, contained gases, rate and amount of flow, form and position of the spring opening are all characteristics of springs, which, while in many cases related to genesis, vary among springs of the same origin. He went on to explain that for that reason the use of this classification, difficulties will arise which are of two types. The first difficulty being that the local structure in the vicinity of springs is difficult to determine because the presence and passage of water facilitates weathering and destroys the evidence again the presence of luxuriant vegetation also tends to conceal the structure. The second difficulty arises through various combinations of structures which may combine to produce a spring. The structure which plays the predominating role should then determine the classification of the spring.

He further stated that the conditions and processes that give rise to springs should be distinguished from those that bring about capillary discharge of groundwater. The reason being that the water of springs and seeps rises under pressure transmitted through the water as it lies as a continuous body in the voids of the rock. On the other hand, capillary discharge is due to molecular attraction between the soil particles and the water, acting against gravity. It takes place because the water is raised from the water table through minute openings in the soil by the force of capillarity and evaporates at or near the land surface. No water is released except by evaporation into the air, whereas the water of springs and seeps forms streams and pools unless the quantity is small and the evaporation excessive.

Rango et al. (2008) carried out a study on the hydrogeochemical study in the main Ethiopian rift: new insights to the source and enrichment mechanism of fluoride. The sampling strategy they adopted took into consideration the previous hydrogeological/geological/geochemical studies of the area. They collected water samples from hot springs, lakes, boreholes, rivers and stored in 100 ml polyethylene bottles after filtering using 0.45 *l*m membrane filters. They performed in situ measurements of pH, EC, and temperature.

Part of their findings was that the geochemical features of water in their study area were extremely variable, ranging from low TDS (and low F) in rivers to very high TDS (and high F) in the rift groundwater wells, hot springs and lakes. The average TDS in the groundwater wells and hot springs were 1,050 and 3,610 mg/l, respectively. TDS was even more variable in lake waters, with values which vary from the fresh water Ziway lake (379 mg/l), brackish water Langano lake (1,377 mg/l) to the saline Shala, Abijata and Chitu lakes (11,563; 52,725 and 64,267 mg/l, respectively). pH ranged from near neutral to alkaline with an extreme value up to 10 was recorded. Different hydrochemical facies were identified on the basis of the Piper classification for the different water types (groundwater wells, geothermal wells, hot springs).

Analyses of major cations (Na, K, Mg, Ca) was carried out using AA spectrometry and anions (F, Cl, SO4) were analyzed by ion chromatography and spectral photometry. When comparing the relative concentration of major ions in the waters they found out that Na was always higher than K, since Na was more abundant than K in the host rocks, and K-minerals in primary volcanic parageneses were more resistant to weathering than Na-minerals (i.e. plagioclase is more alterable than K-feldspar); moreover K is easily stabilized in neo-formation minerals (clay minerals). Mg was lower in concentration than Ca, probably due to the low abundance of Mg in the outcropping rocks. Depletion of Ca and Mg and enrichment in Na and K was observed along the groundwater flow paths, moving from the highlands to the rift axial zone.

Rango et al. (2008) did not relate the high concentration of bicarbonate to calcite dissolution since carbonates were not present in their study area. They concluded that it was induced by magmatic outgassing that is to say CO_2 could upraise along the many faults still active in the rift. Carbon dioxide also increases the water aggressivity, i.e. its capability to trigger water/rock interaction processes thus explaining the positive relationships between HCO_3 and other parameters such as Na, Cl and F.

2.5 Geothermal systems

Sheridan et al. (1980) carried out a research of the Geothermal Resource Evaluation at Castle Hot Spring, Arizona. The Castle Hot Spring was said to be the highest temperature hot spring in the transition zone of the north west of Phoenix. Their main aim was to define the geothermal system that supplies the hot water for Castle Hot Spring. Samples were collected and analysed at approximately one-month intervals for a period of one year at Castle Hot Spring and Henderson Ranch Spring. The small variations noted in the data indicate that rainfall or seasonal temperature variations have no perceptab1e effect on the chemistry or temperature of the springs.

Kreye et al. (1996) stated water chemistry and seasonal variation as ways which can be used to infer the origin and relative age of water. By way of example they stated was that a spring may show distinct seasonal variability in chemistry that correlates with the seasonal precipitation fluctuation, indicating that the spring is recharged directly by infiltration of precipitation. On the other hand they said spring water chemistry contains chemical, isotopic, and thermal signatures which may reveal flow paths and history, for example, the amount of total dissolved solids (TDS), in the spring water compared to the chemistry of nearby surface water, rain water, and well water may indicate the relative subsurface residence time and distance groundwater has traveled before discharging as a spring. Spring water with low TDS (slightly higher than rain or surface water) would suggest that the spring water is from infiltration of local precipitation or fresh surface water and that the source area is of local rather than regional extent.

They further stated that the presence of elevated levels of minute chemical constituents, such as arsenic, fluoride, organic acids, and nitrate, in the spring water provides clues to the origin of the spring water and helps define the location of the source area by association with specific geologic units or land use activities.

On the matter of site investigation Kreye et al. (1996) went on to state that in many cases, the mechanism of spring occurrence will not be obvious from an office assessment and can only be determined by site investigation, that is to say, a site visit enables spring works to be documented and locations identified for monitoring spring flow and raw water quality.

2.6 Water-rock interactions

Mwangi (2013) stated in the study carried out on the application of geochemical methods in geothermal exploration in Kenya that water rock interaction is of importance when it comes to geochemistry because different components and constituents are produced that are of interest to geochemists. The author also stated that geothermal exploration provides a great understanding of the location, nature and origin of the geothermal waters in a geothermal system. Geothermometers are parameters used to determine sub-surface conditions since at particular temperatures, common assemblages of minerals will tend towards equilibrium with a given water chemistry. It has been noted that for certain parameters or ratios of parameters, the relationship between temperature and chemical composition will be stable and predictable.The author used three methods to obtain geochemical samples and they are: Water sampling – which involved the collection of liquid water samples from drilled boreholes and natural springs so as to evaluate origin of the fluids, temperature estimations at depth, predict scaling and corrosion problems; secondly, Fumarole steam and condensate sampling in this case gases and condensates were sampled in order to compute reservoir temperature at depth where the steam is being formed; lastly, Soil gas survey (for Rn-222, CO_2 and temperature) - Rn-222 and CO_2 in the soil are indicators of permeability and possible location of a reservoir.

CHAPTER 3.0 - METHODOLOGY

3.1 General

In order to determine the hydrogeochemistry of the Kasane thermal spring, representative water, sediment and rock samples were collected during the rainy season. Analyses of the water and sediment samples were carried out both in the geochemistry laboratory of the University of Botswana and in the laboratory of the Department of Water Affairs of Botswana. Cations and trace elements of the water and sediment samples were analysed in the geochemistry laboratory of the University of Botswana. Anions of the water samples were analysed in the laboratory of the Department of Water Affairs of Botswana. Anions of the sediments samples were analysed in the geochemistry laboratory of the University of Botswana.

In situ measurements of some physical and chemical parameters of the water were conducted during field investigation. Rock samples were characterized by studying thin-sections at the transmitted light microscope.

3.2 Data Collection

3.2.1 Field investigations

Sixteen (16) water samples, forty nine (49) sediment samples and three (3) rock samples were collected from different sites of the studied area.

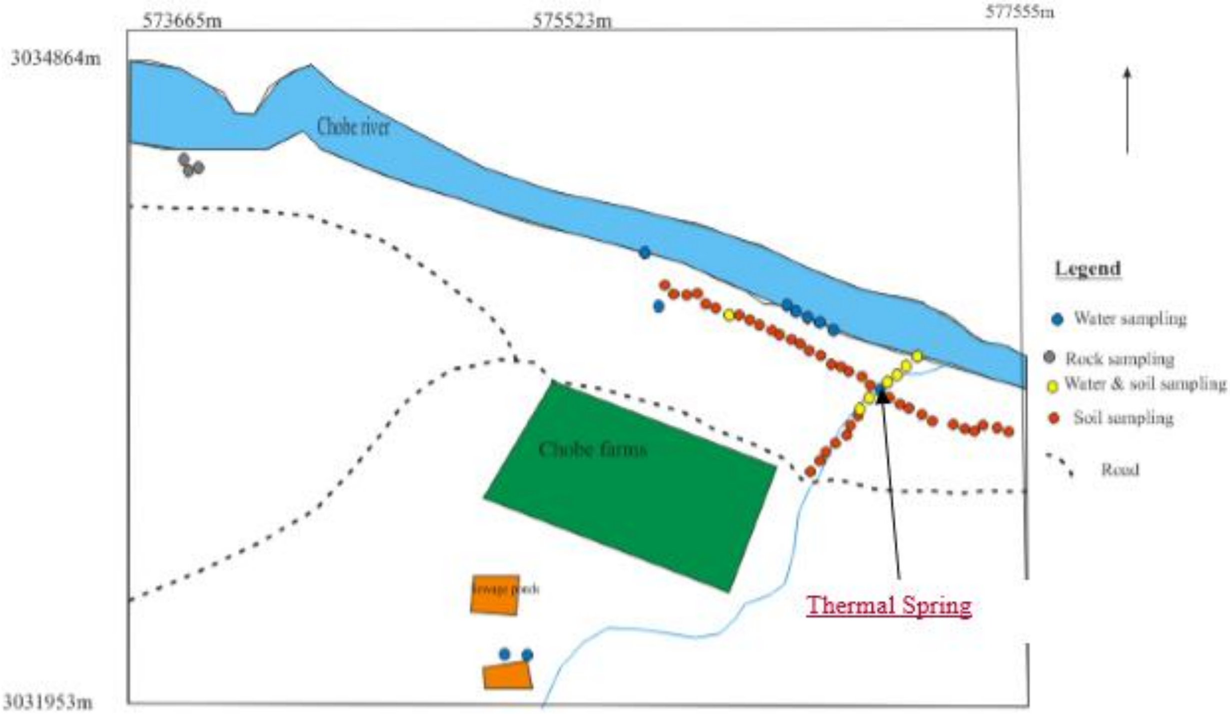


Figure 9. The points of sampling in the study area.

The water samples were collected from the thermal spring, sewage ponds, the river and the pits: one from thermal spring, two from sewage ponds, one from the nearby river water and 12 from the drilled pits. The pits, which were drilled for sediment sampling purposes, were drilled in different directions and at different intervals from the spring; because of this reason, with the exception of the thermal spring sample all the water samples from the pits were obtained from the same points where sediment sampling was done.

The sediment and water samples were obtained in all four directions (north, south, east and west) of the spring at a distance of an interval of 50 m with the spring as the point of origin (Fig. 9 & Fig. 10). The two sewage ponds are located in the upstream side of the thermal spring, while the river is located in the downstream side of the spring. The river is a perennial river.

Figure 10. A tape measure used to measure the 50m interval between sampling points.

The water samples were collected in one litre Polyethylene terephthalate bottles after filtered them through 0.45-µm cellulose filters (Fig. 11). Prior to sampling the bottles were rinsed with samples to be collected. In the field in situ measurements of the water temperature, pH, EC, and TDS were conducted using digital multi-parameter analyser model Hanna. The positions and altitudes of the sampling points (locations) were also determined using Global Positioning System (GPS).

Figure 11. The water samples were filtered and stored

Sediment samples were collected from the pits that were drilled at different directions and different intervals from the springs (Fig. 12). The pits had a dimension of 30 cm by 30 cm and depth of 50cm. One kilogram (kg) sediment samples were collected from each pit using a plastic bag. The positions and altitudes of the pits were determined using Global Positioning System (GPS).

Figure 12. Sediment sample collected and labelled.

Representative rock samples were also collected using a geological hammer during the field work from the area where there is an exposure. The positions and altitudes of the sampling points (location) determined using Global Positioning System (GPS). Hydrochloric acid was used in the field to test the calcite nature of the rocks. Thin-sections of the rocks samples were prepared in the University of Botswana at the cutting and polishing laboratory of the Department of Geology for petrographic investigation.

3.3 Data analyses

3.3.1 Water samples

The water samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), lithium (Li^+), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), fluoride (F^-), phosphate (PO_4^{3-}), nitrite (NO_2^-) and bromine (Br^-). The trace element that were analysed in the water samples were arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni) and zinc (Zn). The water from sewage ponds, river and pits were analysed for comparison with thermal spring water.

All cations and trace elements were analysed using ICP-MS. The method applied for the analysis of anions was ISO 10304 using the ion chromatography. The alkalinity and hardness of water samples were determined using AquaChem software.

Simple descriptive statistical method was utilized for the analyses of the groundwater chemistry data. Besides, AquaChem software, a fully integrated statistical package developed specifically for graphical and numerical analyses of aqueous geochemical data sets was used to process water geochemical data. Piper diagram was prepared to represent and compare water quality data in the area. Gibbs diagram was also used to see the relationship of water composition and aquifer lithological characteristics. In addition, Durov plot, Scatter plot and Pie chart were used for graphical presentation of the results. On the Durov plot; the calcium percentages are plotted along the top scale, following the grid lines extending in a NW-SW direction; the magnesium percentages are plotted following the vertical grid lines; the sodium plus potassium percentages are plotted along the bottom scale, following the grid lines extending in a NE-SW direction; the top triangle is for the anions; the chloride percentages are plotted along the left scale, following the grid lines extending in a NW-SW direction; the sulphate percentages are plotted following the horizontal grid lines; and, the bicarbonate percentages are plotted along the right scale, following the grid lines extending in a NE-SW direction.

3.3.2 Sediments samples

Prior to analytical work for cations and trace elements, the samples were air dried in the laboratory. Out of the total dried samples only 50mg of the samples were taken for the preparation of the solutions that were used for the required analyses (Fig. 13A). The solution of each soil sample was done by digestion or leaching of the sample. The 50 mg sediment samples were digested using 3 acids in different quantities (Fig. 13B): 0.5 ml of HNO_3, 2.5 ml of HF and 0.5 ml of $HClO_4$ because a study carried out by Koki (2005) led to the conclusion that from the different possible treatments of soil samples, the tri-acid mixture (HF, $HClO_4$ and HNO_3) gave the best result, followed by mixture of HCl and HNO_3, and lastly soil leaching using concentrated HCl. The samples were then placed in an ultrasonic cleansing tank at a temperature of 50°C for a period of 2 hours.

A B

Figure 13. A) The sediments samples were weighed using an electric balance: B) Sediments samples being treated with the tri-acid mixture.

The samples where then allowed to cool then they were opened and placed on a digital hot plate SD500 to dry. The temperature of the hot plate was initially at 50°C, then it was increased gradually to a final temperature of 201°C. The drying process took approximately 11 hours.
Drying caused the sediments to solidifying once again and after allowing them to cool, the process of adding acids was repeated. The samples were placed in the ultrasonic cleansing tank once again under the same conditions (Fig. 14).

The samples were dried again (Fig. 15) and afterwards only 2g of nitric acid was added to the samples. They were then placed on the digital hot plate for 2 hours at a temperature of 100°C. Once the samples had dissolved, 8g of distilled water was then added. The samples were then ready for analysis.

Figure 14. The ultrasonic tank.

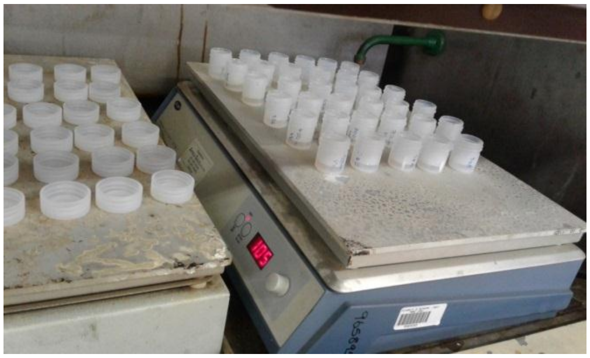


Figure 15. Samples being dried

The soil samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}), and lithium (Li^{+}). The trace element that were analysed in the soil samples were arsenic (As), barium (Ba), cadmium (Cd), Cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni) and zinc (Zn).

For analyses of anions, 24 sediments samples were prepared. For each sediment sample 2g of it was mixed with 25g of distilled water then placed on a flask shaker for 12 hours. This mixture was then filtered in two stages, first using the 110mm filter paper then using the 0.45-µm cellulose filters. To make the eluent the following specifications were followed; 2.2099g of 8mM Hydroxybenzoic acid, 6.183g of 50mM Boric acid powder and 1.3391g of 3.2mM BIS-TRIS were mixed together to make a 2 litres solution using distilled water.

The anions to be determined were the following; chloride (Cl^{-}), sulfate (SO_4^{2-}), nitrate (NO_3^{-}), nitrite (NO_2^{-}), fluoride (F^{-}), phosphate (PO_4^{3-}) and bromide (Br^{-}). The analysis was done using the Shimadzu Ion Chromatograph (HIC-20Asuper).

Simple descriptive statistical method was used for the analyses of the soil chemistry data too.

3.3.3 Rock samples

Representative rock samples were collected during the field campaign. The samples were preliminarily characterized by studying the hand specimen. Thereafter, thin-sections of the rock samples were observed for minerals at the transmitted light microscope using Nikon Eclipse 50i POL microscope at the petrological laboratory of the Department of Geology in the University of Botswana in order to establish the relationship between the geology and the chemistry of the water in the study area.

A B

Figure 16. A) The buehlerlapro slab saw 18 was used to remove the weathered part of the rock samples. B) The rock samples being air dried after they were washed with water and soap.

3.4 Quality Control

The instruments used for analysis were calibrated at the beginning of every analytical run using standards. In addition to that standards were inserted between the samples to correct for any drift in instrument sensitivity. In order to minimise the contamination from other sources the samples were analysed neat, without any dilution. However, samples which detected concentrations above the maximum concentration of the standards were diluted.

In the water analyses, for analytical precision of measured samples, charge balance was calculated using the following equation:

$$\text{Where, E.N (\%)} = \left[\frac{(\text{Sum cations} - \text{Sum anions})}{(\text{Sum cations} + \text{Sum anions})}\right] * 100 \qquad (1)$$

All the measurements are in milli equivalents per litre.

CHAPTER 4.0 – RESULTS

4.1 Hydrochemistry

4.1.1 Physico-chemical Parameters

As stated on the methodology section of this paper, pH, electrical conductivity, total dissolved solids and temperature of the water were measured in-situ using a digital multi-parameter analyser of the Hanna model. The results are given in the Table 1 below. The water is acidic to alkaline and soft to very hard. pH ranges from 6.33 to 9.12 with an average of 7.27. The maximum value of pH was measured 750 m west of the spring and minimum was measured in the centre of the river. Electrical conductivity and total dissolved solids range from 82µS/cm to 22320µS/cm and 36.72 mg/l to 14476.92 mg/l with a mean value of 5172.75µS/cm and 3140.72 mg/l, respectively. The highest electrical conductivity value is 22320µS/cm measured 50m north of the spring. From north side of the spring all the measured electrical conductivity values are above 10000µS/cm. The measured electrical conductivity values west of the spring and at the sewage have low values mostly below 1500 µS/cm. There is no record of electrical conductivity in the east and south directions as the pits drilled in those directions did not yield any water. The temperature of the water samples was recorded between 25 °C and 49.7 °C with an average value of 28.99 °C. The maximum temperature was measured in the spring and the lowest was 1197.5m west of the spring.

Table 1. Physico-chemical parameters of water.

Sample ID	Sample Type, Location and Direction*	EC (µS/cm)	pH	Temp (°C)	TDS (mg/l)
W1	Thermal spring	11700	7.65	49.7	6957.95
W2	GW 50m N	22320	7.89	35	14476.92
W3	GW 100m N	16800	7.82	29.8	10683.2
W4	GW 150m N	11820	8.03	28	7047.6
W5	GW 200m N	11010	8.65	26.5	6282.24
W6	GW 300m W	124	6.71	26.3	39.65
W7	GW 350m W	85	6.77	26.5	39.56
W8	GW 400m W	85	6.51	27.1	39.4
W9	GW 500m W	82	6.49	26	36.72
W10	GW 550m W	91	6.78	27	41.84
W11	GW 750m W	1202	9.12	26.2	596.42
W12	GW 1050m W	5437	6.89	25.9	3131.46
W13	GW 1197.5m W	82	6.69	25	37.73
W14	River	83	6.33	26.1	37.98
W15	Sewage 1	1430	6.96	29.7	607.95
W16	Sewage 2	413	7.08	29	194.94
Minimum		82	6.33	25	36.72
Maximum		22320	9.12	49.7	14476.92
Mean		5172.75	7.27	28.99	3140.723

Where GW is groundwater.

*: Direction and distance from the thermal spring.

4.1.2 Quality Control

The electro neutrality (E.N. %) values of all samples were determined using Aquachem software. 75% of the samples had an EN value less than 5% which is generally accepted. A perfect analysis was supposed to reach a charge balance of 0%. The analysis however did not yield such a result as different instruments were used for the analysis of ions. This may also be a result of incorrect dilutions of samples, having very dilute samples or contamination of samples.

4.1.3 Hardness

Hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, both calcium and magnesium.

Hardness of water is defined as its content of metallic ions which reacts with sodium soaps to produce solid soaps or scummy residue and which react with negative ions, when the water is evaporated in boilers, to produce solid boiler scale (Camp, 1963). It is predominantly caused by divalent cations such as calcium, magnesium, alkaline earth metal such as iron, manganese, strontium, etc. It is a water quality indication of the concentration of alkaline salts in water, mainly calcium and magnesium. Hardness is normally expressed as the total concentration of Ca^{2+} and Mg^{2+} as milligrams per litre equivalent of $CaCO_3$. The total hardness is defined as the sum of calcium and magnesium concentrations, both expressed as $CaCO_3$ in mg/l. It can be determined by substituting the concentration of Ca^{2+} and $Mg^{2+,}$ expressed in milligrams per litre, in the expression:

$$\text{Total Hardness} = 2.5\,(Ca^{2+}) + 4.1\,(Mg^{2+}) \qquad (2)$$

Each concentration is multiplied by the ratio of the formula weight of $CaCO_3$ to the atomic weight of the ion; hence the factors 2.5 and 4.1 are included in the hardness relation.

Table 2: Water hardness classifications (reported as CaCO3 equivalents) used by the U.S. EPA (EPA, 1986).

Classification	$CaCO_3$ equivalent (mg/L)
Soft	<75
Moderately hard	75–150
Hard	150–300
Very hard	>300

Table 3: Hardness values of the water samples.

Sample	Sample location	Total Hardness as CaCO3 in mg/l
W1	Spring	432.24
W2	50m N of the spring	1022.74
W3	100m N of the spring	838.88
W4	150m N of the spring	427.78
W5	200m N of the spring	196.01
W6	300m W of the spring	32.54
W7	400m W of the spring	27.73
W8	450m W of the spring	26.59
W9	500m W of the spring	26.53
W10	550m W of the spring	26.91
W11	750m W of the spring	87.04
W12	1050m W of the spring	261.81
W13	1197.5m W of the spring	26.17
W14	River	26.75
W15	Sewage 1	32.77
W16	Sewage 2	39.61

Generally, the hardness of the water in the study area varies from soft to very hard. All the water samples north of the thermal spring reveal that the water is very hard to hard whereas the water samples west of the thermal spring indicates that water is soft. The sewage water from upstream side, which is south of the thermal spring, and the river water from downstream side are both soft water.

4.1.4 Alkalinity

The alkalinity of water is a characteristic that computes its measure of neutralizing acids. Alkalinity of natural water is defined by the presence of two forms of the carbonate ions: HCO_3^- and CO_3^{2-} that act as a buffer system. It is measured in mg/l of $CaCO_3$. Naturally occurred alkalinity is in the range from 400 to 500 mg/l. It provides a qualitative overview to the sensitivity or susceptibility of water to acidification.

Table 4: Classification of water samples based on susceptibility to acidification according to the Massachusetts acid rain monitoring project (Godfrey et al., 1996).

Classification	Alkalinity (mg/l of $CaCO_3$)
Critical	Below 2
Endangered	Between 2 and 5
Highly sensitive	Between 5 and 10
Sensitive	Between 10 and 20
Not sensitive	Above 20

The alkalinity of the water samples was determined and the result is given in the Table 5 below. Accordingly, the alkalinity of the water samples range from 31.58 to 446.92 mg/l of $CaCO_3$. Very high values are observed north of the thermal springs and in one of the sewage sample. According to the above classification scheme (Table 4), all the waters of the studied area are less susceptible to acidification.

Table 5. Alkalinity of the water samples.

Sample	Sample location	Alkalinity (mg/l of $CaCO_3$)
W1	Spring	90.55
W2	50m N of the spring	446.92
W3	100m N of the spring	259.34
W4	150m N of the spring	333.32
W5	200m N of the spring	256.59
W6	300m W of the spring	33.38
W7	400m W of the spring	33.55
W8	450m W of the spring	33.22
W9	500m W of the spring	31.58

W10	550m W of the spring	34.86
W11	750m W of the spring	116.5
W12	1050m W of the spring	98.75
W13	1197.5m W of the spring	32.56
W14	River	32.89
W15	Sewage 1	350.22
W16	Sewage 2	72.26

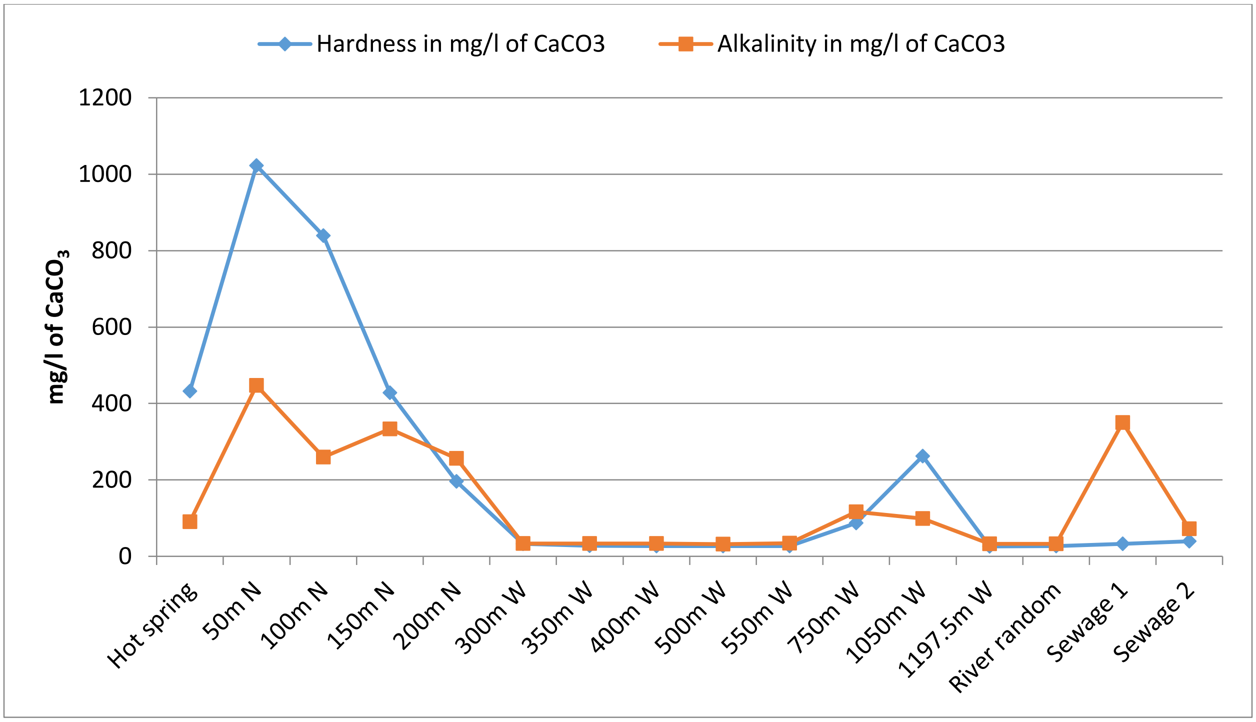


Figure 17. The alkalinity and hardness of the water samples

4.1.5 Water type

Categorizing water on the basis of percentage composition of major cations and anions has a paramount importance in the understanding of the hydrochemical facies of the groundwater in a certain area. To classify water on the basis of these criteria, a systematic graphic presentation is essential. Among these graphical presentation, Piper tri-linear diagram is the most useful method. It evaluates the evolution of water and relationship between rock types and water composition

(Ravikumar et al., 2015). In this specific research, classifying and grouping was done for all the samples that were collected in the field. The major cations and anions species plotted on this diagram are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, CO_3^{2-}, HCO_3^- and SO_4^{2-}. The chemical analysis results of the water samples from the study area are plotted in this diagram using Aquachem software (Fig 18) and the result is summarized and given in Table 6 below. Accordingly, with the exception of the sewage water and one water sample from west of the thermal spring, three major water types are recognized in the studied area: Ca-Mg-Na-HCO_3, Na-Cl-SO_4, and Na-SO_4-Cl; constituting 38%, 31%, and 13% of the total water samples, respectively. The two sewage water samples are Na-HCO_3-Cl and Na-Cl-HCO_3-SO_4 types, while one sample from west of the thermal spring shows Ca-Mg-HCO_3.

Table 6. Water types of the studied area.

Sample ID	Sample location	Water type
W1	Spring	Na-Cl-SO_4
W2	50m N of spring	Na-Cl-SO_4
W3	100m N of spring	Na-Cl-SO_4
W4	150m N of spring	Na-Cl-SO_4
W5	200m N of spring	Na-Cl-SO_4
W6	300m W of spring	Ca-Mg-Na-HCO_3
W7	350m W of spring	Ca-Mg-Na-HCO_3
W8	400m W of spring	Ca-Mg-Na-HCO_3
W9	500m W of spring	Ca-Mg-Na-HCO_3
W10	550m W of spring	Ca-Mg-HCO_3
W11	750m W of spring	Na-SO_4-Cl
W12	1050m W of spring	Na-SO_4-Cl
W13	1197.5m W of spring	Ca-Mg-Na-HCO_3
W14	River	Ca-Mg-Na-HCO_3
W15	Sewage 1	Na-HCO_3-Cl
W16	Sewage 2	Na-Cl-HCO_3-SO_4

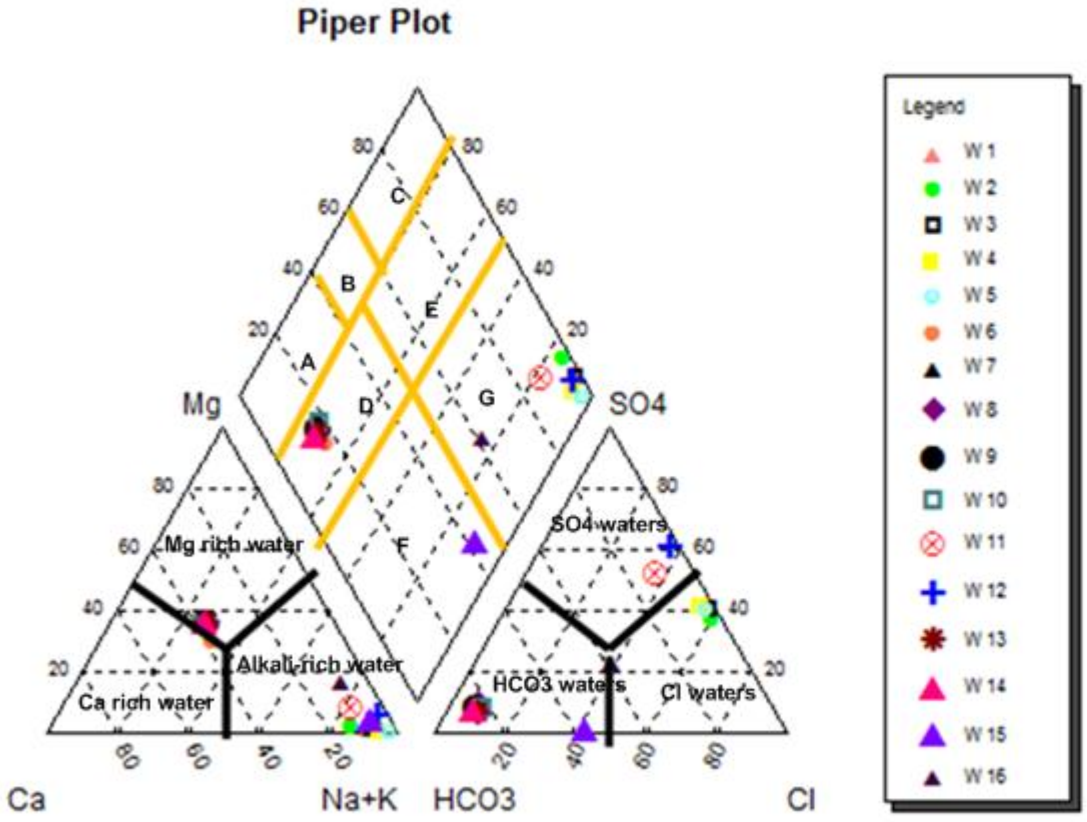


Figure 18. Piper plot for the water samples

Table 7. Classification of water types on a piper plot according to Ravikumar et al (2015).

Normal Earth Alkaline water	Earth Alkaline water with increased portions of alkalies	Alkaline water
A) with prevailing HCO3	D) with prevailing HCO3	F) with prevailing HCO3-
B) with prevailing HCO3 and SO4 or Cl	E) with prevailing SO4 and Cl	G) with prevailing SO4 -Cl
C) with prevailing SO4 or Cl		

4.1.6 Classification techniques for geochemical processes

A durov plot is used to show plausible hydrochemical processes occurring within the hydrological system. The Durov is advantageous over the piper diagram in revealing some geochemical processes that could affect groundwater genesis (Ravikumar et al., 2015).

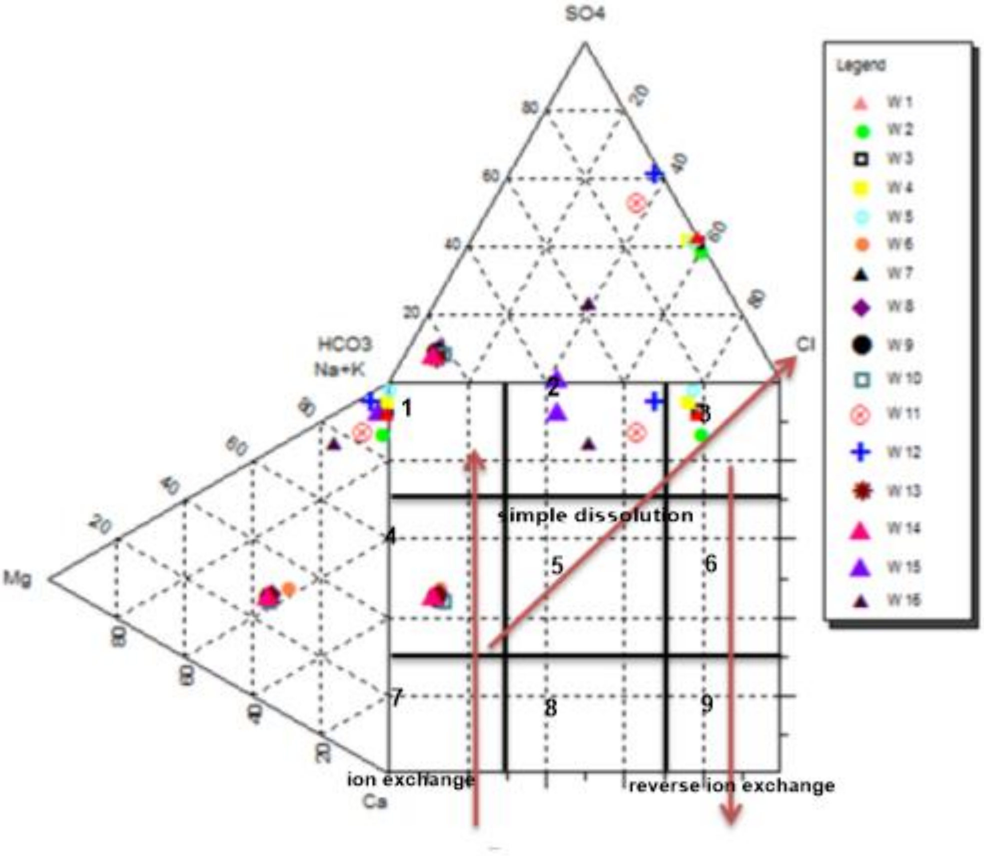


Figure 19. Durov plot showing major ions

The water samples fall within fields 2, 3 and 4. According to Lloyd & Heathcoat (1985) the water samples which fall in field 3, field 4 and field 2 depict simple dissolution or mixing and ion exchange, respectively.

4.1.7 Major Ions Compositions

The summarized results of the chemical composition of the analysed water samples are given in Table 8 below.

The dominant cations in the water samples are sodium and calcium. The concentration of Na^+ ranges from 3.491 mg/l to 4308 mg/l having a mean value of 1042.12 mg/l. K^+ ranges from 1.493 mg/l to 25.42 mg/l with a mean value of 8.869 mg/l. Ca^{2+} ranges from 5.01 mg/l to 349.8 mg/l with a mean value of 70.4709 mg/l while Mg^{2+} ranges from 2.791 mg/l to 41.72 mg/l with a mean value of 10.869 mg/l. Cation content indicates that 43.75 % of the water samples follows the following trend; $Ca^{2+} > Na^+ > Mg^{2+} > K^+ > Li^+$. The remaining samples follow 5 different trends; 18.75% shows $Na^+ > Ca^{2+} > K^+ > Mg^{2+} > Li^+$; 18.75% of the samples shows $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Li^+$; and, the last 3 samples which take up 6.25 % of the total number of samples are each unique and follow the following trends $Na^+ > Mg^{2+} > Ca^{2+} > K^+ > Li^+$, $Na^+ > K^+ > Ca^{2+} > Mg^{2+} > Li^+$ and $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Li^+$. Generally, based on the mean values of the chemical parameters, the cations were in the order of abundance as $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Li^+$.

Among anions, HCO_3^- ranges from 38.5 mg/l to 544.9 mg/l with mean value of 167.044 mg/l while CO_3^{2-} ranges from 0 mg/l to 25.2 mg/l with mean value of 2.413 mg/l. The concentration of SO_4^{2-} ranges from 2.39 mg/l to 6369.31 mg/l with a mean value of 1469.98 mg/l while Cl^- ranges from 1.93 mg/l to 7570.65 mg/l with mean value of 1505.72 mg/l. The concentration of NO_3^- ranges from 0 mg/l to 20.23 mg/l with mean value of 2.4 mg/l while NO_2^- ranges from 0 mg/l to 0.05 mg/l with mean value of 0.009 mg/l. F^- ranges from 0.02 mg/l to 5.36 mg/l with mean value of 1.354 mg/l. PO_4^{3-} concentration ranges from 0 mg/l to 45.6 mg/l with mean value of 3.55 mg/l. Generally based on the mean values of the chemical parameters, the anions were in the order of abundance as $Cl^- > SO_4^{2-} > HCO_3^- > PO_4^{3-} > Br^- > CO_3^{2-} > NO_3^- > F^- > NO_2^-$.

There is a variation of chloride concentrations of the water samples with the lowest concentration observed from the river and the highest observed 50m north of the spring. The chloride concentration increases towards the spring from both the north and west directions. However, the concentration is lowest in the river sample. Chloride concentration in the water samples was not monitored east and south of the spring as there were no samples obtained in those directions.

The samples obtained from the spring and from north of the spring measured the highest levels of sulphate compared to the rest of the samples. These concentrations were all above 2000 mg/l. Lower concentration levels were obtained mostly from samples west of the spring.

The highest nitrate level was from the sewage water sample. Generally the nitrate concentration decreased towards the spring from the directions which were analysed for nitrates (west and north).

Table 8. Summarized results of the analysed water samples (mg/l).

ID	Type/direction*	Cl^-	SO_4^{2-}	NO_3^-	F^-	CO_3^{2-}	HCO_3^-	NO_2^-	PO_4^{3-}	Br^-	Ca^{2+}	K^+	Li^+	Mg^{2+}	Na^+
W1	Thermal spring	3452.21	3398.47	1.05	2.96	0	110.4	0	0	7.95	151.74	15.664	0.4759	12.94	1983.6
W2	50m N	7570.65	6369.31	0	3.63	0	544.9	0	0	15.43	349.8	25.42	0.6286	36.22	2649
W3	100m N	5321.91	5047.33	1.87	3.03	0	316.2	0	0	10.8	294.81	19.868	0.5451	24.92	4308
W4	150m N	3321.67	3321.26	0.3	5.11	0	406.4	0	0	7.78	154.82	15.96	0.4307	9.989	3105
W5	200m N	3069.53	2921.92	6.97	5.36	13.4	285.6	0	0	6.97	67.34	16.694	0.4296	6.756	2882
W6	300m W	2.43	3.22	0.42	0.02	0	40.7	0.05	0	0.004	7.287	2.052	0.0021	3.483	5.847
W7	350m W	2.21	3.09	0.46	0.04	0	40.9	0.03	0	0.02	5.812	1.694	0.0015	3.208	3.82
W8	400m W	2.22	3.44	0.35	0.03	0	40.5	0	0	0.001	5.554	1.493	0.0015	3.085	3.966
W9	500m W	2.04	2.92	0.37	0.03	0	38.5	0.03	0	0	5.484	1.615	0.0016	3.119	3.491
W10	550m W	3.02	2.98	0.43	0.05	0	42.5	0.01	0	0	5.633	1.563	0.0022	3.116	3.504
W11	750m W	167.74	317.83	0.59	0.4	25.2	90.8	0	0	0.19	18.886	9.467	0.0411	9.677	186.28
W12	1050m W	935.27	2078.69	3.88	0.36	0	120.4	0	0	1.65	36.04	2.457	0.0128	41.72	1349
W13	1197.5m W	2.32	2.39	0.42	0.04	0	39.7	0.03	0	0	5.346	1.638	0.0015	3.106	3.634
W14	River random	1.93	2.72	0.34	0.03	0	40.1	0	0	0	5.45	1.601	0.0016	3.187	3.696
W15	Sewage 1	183.93	2.97	0.72	0.47	0	427	0	45.6	0.14	8.523	10.476	0.0027	2.791	134.62
W16	Sewage 2	52.48	41.17	20.23	0.1	0	88.1	0	11.2	0.02	5.01	14.24	0.0061	6.58	48.46
Minimum		1.93	2.39	0	0.02	0	38.5	0	0	0	5.01	1.493	0.0015	2.791	3.491
Maximum		7570.65	6369.31	20.23	5.36	25.2	544.9	0.05	45.6	15.43	349.8	25.42	0.6286	41.72	4308
Mean		1505.72	1469.98	2.4	1.354	2.413	167.044	0.009	3.55	3.185	70.4709	8.86888	0.16154	10.8686	1042.12

*: Direction and distance from the thermal spring.

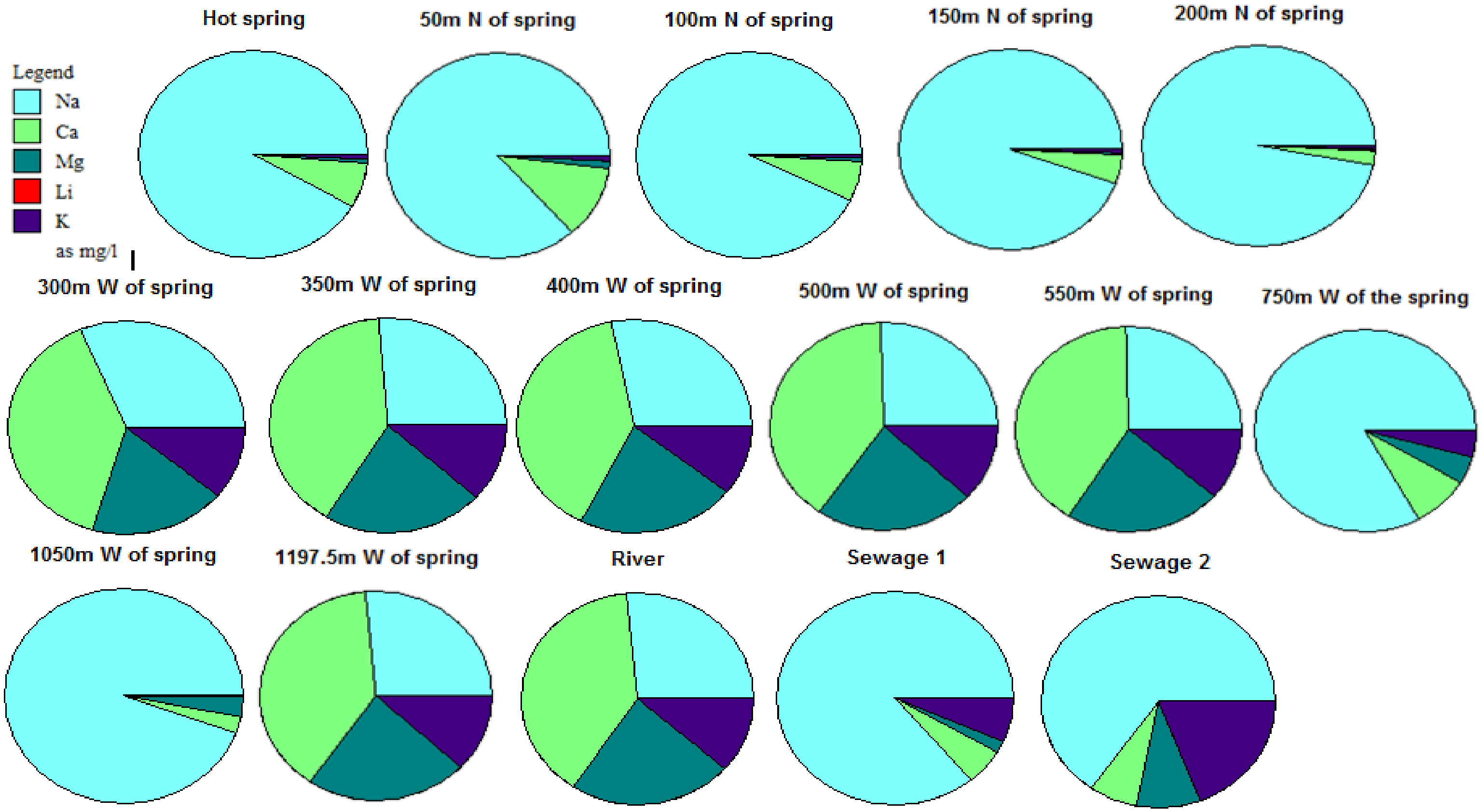


Figure 20. Major cations in the water samples.

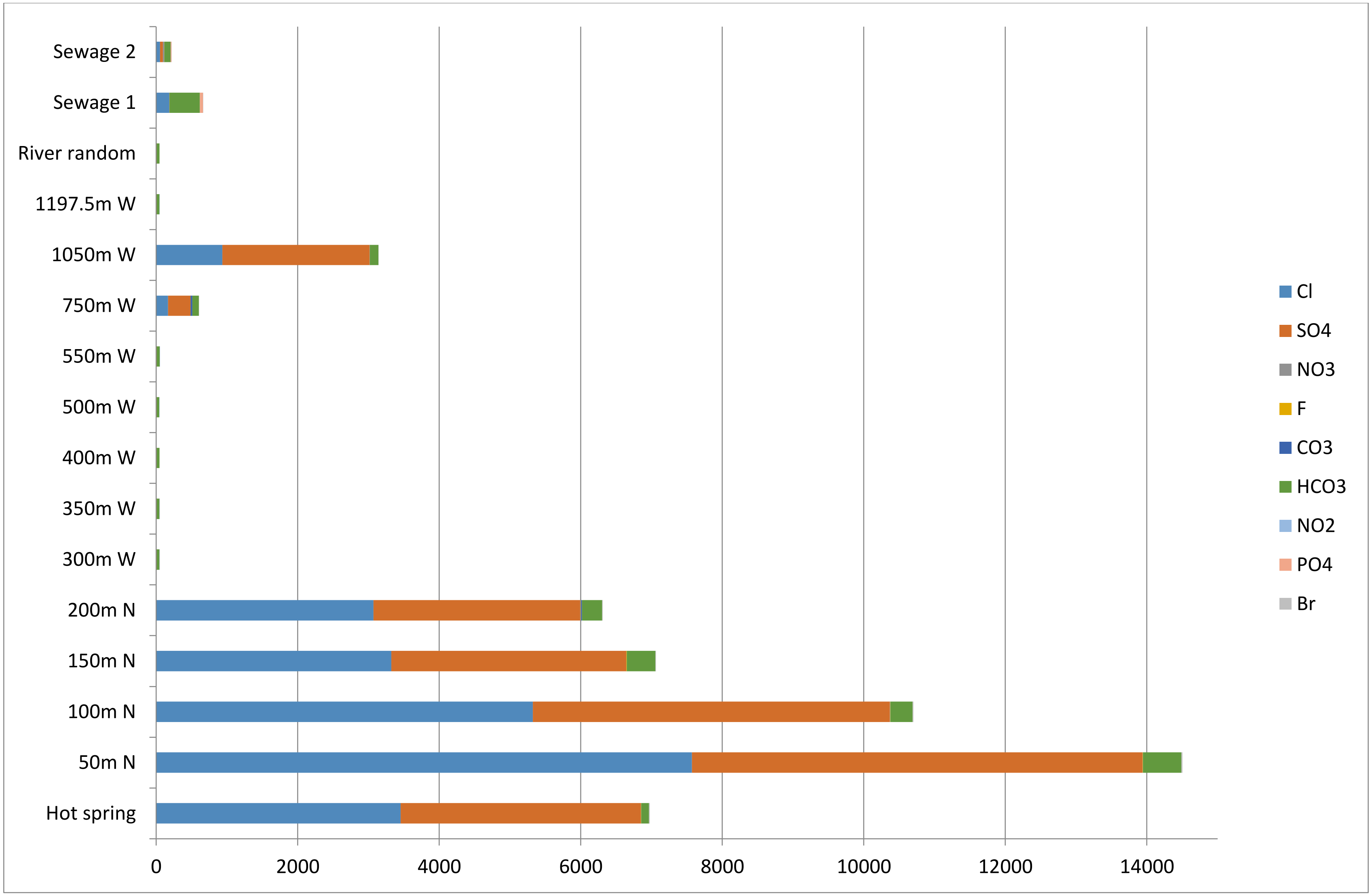


Figure 21. Major anions in the water samples.

4.1.8 Trace elements

As stated in the methodology section of this paper, the water samples were also analysed for some trace elements: As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The results of the analyses of these trace elements is summarized and given in the Table 9 below. Among these trace elements, Ni is the dominant constituents in the water of the study area. Its concentration ranges from 0.3219 mg/l to 2.288 with mean value of 0.95 mg/l. Fe, Pb, Mn, Zn, and Ba are the major trace elements that are found constituting the water following Ni having concentration of 0.12 mg/l, 0.08mg/l, 0.05mg/l, 0.03mg/l and 0.03mg/l, respectively. As, Cd, Co, Cr and Cu are found having concentration less than 0.001 mg/l.

Table 9: Summarized results of some of the analysed trace elements in water samples (mg/l).

ID	Type/Direction*	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
W1	Thermal spring	0.0001	0.0134	0.0055	0.0014	0.001	0.0043	0.0014	0.0893	1.652	0.165	0.041
W2	50m N	0.0033	0.0354	0.0075	0.0029	0.0001	0.0041	0.0249	0.5172	2.228	0.0819	0.0396
W3	100m N	0.0032	0.053	0.0052	0.0004	0.0004	0.0034	0.0062	0.0076	0.8354	0.0865	0.0334
W4	150m N	0.0097	0.0257	0.0102	0.0013	0.0002	0.0034	0.0036	0.0491	2.288	0.0362	0.0493
W5	200m N	0.0067	0.028	0.0034	0.0004	0.0005	0.0014	0.0019	0.0713	1.766	0.0671	0.0423
W6	300m W	0.0061	0.025	0.0011	0.0018	0.0005	0.0027	0.0787	0.003	0.4447	0.1	0.0305
W7	350m W	0.001	0.0242	0.0024	0.0004	0.0002	0.0046	0.2102	0.001	0.424	0.032	0.0291
W8	400m W	0.001	0.0234	0.0062	0.0035	0.0002	0.0044	0.2517	0.0009	0.4666	0.2121	0.0214
W9	500m W	0.0037	0.0187	0.0033	0.0025	0.0002	0.004	0.0509	0.0003	0.4225	0.1114	0.0302
W10	550m W	0.0005	0.0278	0.0077	0.0013	0.0015	0.0043	0.6987	0.0017	0.5858	0.0252	0.0263
W11	750m W	0.004	0.0202	0.0107	0.0011	0.0004	0.0025	0.0168	0.0003	1.13	0.0297	0.0324
W12	1050m W	0.0007	0.0539	0.0038	0.0001	0	0.0036	0.0057	0.0002	0.3219	0.0247	0.0436
W13	1197.5m W	0.0014	0.0234	0.0021	0.0018	0	0.0046	0.3013	0.0011	0.4779	0.0143	0.0227
W14	River random	0.0034	0.0248	0.0032	0.0004	0.0001	0.0045	0.1525	0.0006	0.4873	0.0627	0.0029
W15	Sewage 1	0.0036	0.0028	0.0181	0	0.0002	0.0024	0.0292	0.0014	0.7496	0.028	0.0424
W16	Sewage 2	0.0018	0.028	0.0035	0.0023	0.0001	0.0031	0.0099	0.0015	0.8402	0.1546	0.0341
Minimum		0.0001	0.0028	0.0011	0	0	0.0014	0.0014	0.0002	0.3219	0.0143	0.0029
Maximum		0.0097	0.0539	0.0181	0.0035	0.0015	0.0046	0.6987	0.5172	2.288	0.2121	0.0493
Mean		0.00314	0.02673	0.00587	0.00135	0.00035	0.00358	0.11523	0.04666	0.94499	0.07696	0.03258

*: Direction and distance from the thermal spring.

4.2 Geochemistry

4.2.1 Sediments

As it was mentioned in the methodology parts the sediments were analysed for major cations, major anions and some trace elements. The same cations and trace elements that were analysed for the water samples were also analysed in the sediment samples and with exception of bicarbonate and carbonate, seven of the anions analysed in the water samples were also analysed in the sediments samples. The data generated for the sediment samples are given in Table 10, 11 and 12 and are discussed below.

The results of the analysis indicate that the concentration of Na^+ ranges from 0.1 mg/l to 25.34 mg/l with mean value of 3.438 mg/l and K^+ ranges from 0.494 mg/l to 11.66 mg/l with mean value of 2.650 mg/l. Ca^{2+} ranges from 0.1387 mg/l to 37.7 mg/l with mean value of 3.067 mg/l while Mg^{2+} ranges from 0.111 mg/l to 7.21 mg/l with mean value of 1.436 mg/l. Li^+ ranges from 0.003 mg/l to 0.046 mg/l with mean value of 0.010 mg/l. Based on the mean values of the chemical parameters, the cations were in the order of abundance as $Na^+ > Ca^{2+} > K^+ > Mg^{2+} > Li^+$.

Table 10: Summarized results of the analysed sediment samples for cations (mg/l).

ID	Direction*	Ca^{2+}	K^+	Li^+	Mg^{2+}	Na^+
S1	50m N	10.66	11.66	0.046	4.88	17.65
S2	100m N	7.51	6.093	0.0286	2.873	25.34
S3	150m N	0.5537	0.6386	0.0038	0.1604	1.357
S4	200m N	1.049	2.416	0.0105	1.007	0.9379
S5	50m E	0.5376	1.228	0.0042	0.1516	1.009
S6	100m E	0.5349	2.655	0.0088	0.5572	0.9928
S7	150m E	1.176	3.547	0.022	1.971	4.054

S8	200m E	18.23	8.844	0.0295	5.93	10.9
S9	250m E	9.749	4.948	0.0161	3.574	6.363
S49	300m E	2.633	2.705	0.0135	1.666	3.87
S10	350m E	6.972	2.733	0.0148	2.177	2.805
S11	400m E	1.845	3.132	0.0117	2.103	4.135
S12	450m E	3.081	3.914	0.0146	3.23	3.317
S13	500m E	3.653	3.813	0.0123	3.182	4.857
S14	550m E	5.4	3.751	0.0162	4.543	7.813
S15	600m E	37.7	3.674	0.0222	7.21	6.795
S16	50m S	1.808	5.008	0.0086	0.7586	3.305
S17	100m S	0.7566	1.722	0.0037	0.3735	2.464
S18	150m S	0.7597	1.695	0.0035	0.3651	2.424
S19	200m S	5.294	7.182	0.0179	3.718	8.678
S20	250m S	3.174	3.389	0.0049	1.139	2.627
S21	300m S	3.968	4.71	0.0112	2.616	4.556
S22	350m S	4.657	3.747	0.0111	2.477	6.7
S23	400m S	2.307	5.233	0.0121	3.153	4.783
S24	450m S	2.485	4.565	0.0081	2.472	2.146
S25	50m W	0.7858	2.298	0.0049	0.648	3.268
S26	100m W	0.1902	0.7339	0.0032	0.1872	3.27

S27	150m W	0.4219	1.311	0.004	0.4011	0.4777
S28	200m W	0.2197	0.6479	0.0027	0.2204	0.14
S29	250m W	0.1879	0.6725	0.0029	0.2282	0.26
S30	300m W	0.2723	0.7119	0.0029	0.1696	0.5794
S31	350m W	0.1387	0.5919	0.0026	0.1621	0.1
S32	400m W	0.1481	0.6259	0.0026	0.1734	0.206
S33	450m W	0.3064	0.9063	0.0041	0.2325	0.433
S34	500m w	0.2523	1.033	0.0043	0.2479	0.14
S35	550m w	0.8739	1.673	0.0073	0.7639	4.151
S36	600m W	3.83	1.47	0.0094	0.7384	3.831
S37	650m W	1.393	1.534	0.0069	0.5975	3.785
S38	700m W	0.3154	1.109	0.005	0.31	1.337
S39	750m W	2.286	1.806	0.0161	1.082	2.609
S40	800m W	0.319	1.361	0.0047	0.2746	0.7636
S41	850m W	0.2118	1.073	0.0032	0.1398	0.6649
S42	900m W	0.2289	0.9547	0.0039	0.1999	0.4135
S43	950m W	0.1728	1.065	0.004	0.2153	0.3268
S44	1000m W	0.2904	1.361	0.0048	0.274	0.4302
S45	1050m W	0.1867	1.119	0.0038	0.1767	0.365
S46	1100m W	0.2518	1.092	0.004	0.2094	0.3574

S47	1150m W	0.3527	1.166	0.0046	0.2927	0.4781
S48	1197.5m W	0.15	0.4936	0.003	0.1113	0.2163
Minimum		0.1387	0.4936	0.0026	0.1113	0.1
Maximum		37.7	11.66	0.046	7.21	25.34
Average		3.066922	2.649229	0.009608	1.435578	3.4384

*: Direction and distance from the thermal spring.

The analysis of the anions indicates that there is no PO_4^{3-} and NO_2^- present in the sediment samples. The concentrations of F^- range from 0 mg/l to 1.463 mg/l with a mean value of 0.232 mg/l. Cl^- concentrations range from 0.622 mg/l to 923.5 mg/l with a mean value of 84.103 mg/l. Br^- concentration was only present in only one sample and therefore ranged from 0 mg/l to 1.626 mg/l with a mean value of 0.068 mg/l. The concentrations of NO_3^- range from 0 mg/l to 10.064 mg/l with a mean value of 1.116 mg/l. SO_4^{2-} concentrations range from 0 mg/l to 1883.9 mg/l with a mean value of 347.44 mg/l. Based on the mean values of the chemical parameters, the anions were in the order of abundance as $SO_4^{2-} > Cl^- > NO_3^- > F^- > Br^- > NO_2^- > PO_4^{3-}$.

Table 11. Summarized results of the analysed sediment samples for anions (mg/l).

ID	Direction *	PO_4^{3-}	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}
S1	50m W	0	0.61	109.4	0	0	1.485	84.624
S2	100m W	0	0	1.754	0	0	0	0
S3	150m W	0	0	2.477	0	0	0	1.992
S4	200m W	0	0	0.622	0	0	0	0

S5	300m W	0	0	45.6	0	0	0	35.076
S6	400m W	0	0	0.855	0	0	0	0
S7	500m W	0	0	1.165	0	0	0	0
S8	50m N	0	0	275.6	0	0	0	1883.9
S9	100m N	0	1.462	923.5	0	1.626	0	901.5
S10	150m N	0	0	44	0	0	1.888	42.251
S11	200m N	0	0	2.136	0	0	3.305	15.594
S12	50m S	0	0	26.4	0	0	0	217.8
S13	100m S	0	0	23.4	0	0	0	866.3
S14	150m S	0	0	118.5	0	0	0	144.972
S15	200m S	0	0.705	121	0	0	0	1529.4
S16	300m S	0	1.212	9.231	0	0	1.479	616.2
S17	400m S	0	0.447	35.1	0	0	0	90.46
S18	50m E	0	0	74.3	0	0	10.064	60.555
S19	100m E	0	0	1.724	0	0	0	0
S20	150m E	0	0.65	29.7	0	0	3.372	145.402
S21	200m E	0	0	20.7	0	0	1.619	692.9
S22	300m E	0	0	33.4	0	0	0	428.6
S23	400m E	0	0	75.7	0	0	0	480.7
S24	500m E	0	0.476	42.2	0	0	3.583	100.234

Minimum	0	0	0.622	0	0	0	0
Maximum	0	1.462	923.5	0	1.626	10.064	1883.9
Average	0	0.23175	84.10267	0	0.06775	1.116458	347.4358

*: Direction and distance from the thermal spring.

Among the analysed trace elements Fe, Ni and Pb are the ones that are found having dominant concentrations: the concentration of Fe ranges from 1.74 mg/l to 51.96 mg/l with mean value of 14.019 mg/l, Ni ranges in concentration from 0.002 mg/l to 1.163 mg/l with mean value of 0.316 mg/l and the concentration of Pb ranges from 0.026 mg/l to 0.827 mg/l with mean value of 0.278 mg/l. All the remaining analysed trace elements have a mean concentration below 0.2 mg/l. Based on the mean values of the chemical parameters, the trace elements were in the order of abundance as Fe > Ni > Pb > Ba > Mn > Zn > As > Cu > Cr > Co > Cd.

Table 12. Summarized results of the analysed sediment samples for some trace elements (mg/l).

ID	Direction*	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S1	50m N	0.2211	0.6208	0.0676	0.0677	0.0807	0.1412	51.96	0.5508	0.1093	0.4786	0.2677
S2	100m N	0.4689	0.2829	0.0447	0.0298	0.0429	0.0551	26.51	0.3214	0.0332	0.3551	0.0413
S3	150m N	0.1621	0.0446	0.0109	0.0082	0.0134	0.0046	2.409	0.0767	0.5632	0.2887	0.0049
S4	200m N	0.0035	0.1363	0.0067	0.0143	0.03	0.0107	9.894	0.0782	0.138	0.4315	0.1133
S5	50m E	0.006	0.0968	0.0005	0.0086	0.0109	0.0045	1.74	0.0345	0.0591	0.2141	0.0444
S6	100m E	0.0059	0.1451	0.0021	0.0141	0.0146	0.0116	6.865	0.0839	0.2935	0.6802	0.1997
S7	150m E	0.1541	0.2015	0.0173	0.0245	0.0302	0.0259	16.86	0.1665	0.2609	0.674	0.0984
S8	200m E	0.0505	0.4149	0.0143	0.0327	0.0451	0.0681	33.13	0.3105	0.0347	0.4694	0.1564
S9	250m E	0.1703	0.3226	0.0199	0.0318	0.0455	0.0684	29.22	0.2797	0.2316	0.4339	0.0012
S49	300m E	0.136	0.3907	0.0147	0.0185	0.0459	0.0388	19.43	0.2441	0.1039	0.1874	0.0707
S10	350m E	0.0361	0.1854	0.0082	0.0196	0.0336	0.0406	20.52	0.3183	0.0641	0.1845	0.0026
S11	400m E	0.0968	0.1758	0.0126	0.0228	0.0298	0.0438	23.61	0.3037	0.0488	0.1921	0.0167
S12	450m E	0.0086	0.1991	0.0126	0.0278	0.0403	0.0621	34.01	0.2918	0.3464	0.3063	0.0173

S13	500m E	0.1397	0.2768	0.0195	0.0376	0.0373	0.0648	31.93	0.4598	1.1114	0.2776	0.0224
S14	550m E	0.4498	0.2799	0.0468	0.0395	0.04-38	0.081	39.46	0.4397	0.244	0.0573	0.0078
S15	600m E	0.0846	0.3583	0.0179	0.0394	0.0487	0.0898	41.23	0.9353	0.9265	0.4186	0.0855
S16	50m S	0.0267	0.2902	0.0029	0.018	0.0176	0.0216	9.574	0.1134	0.2894	0.4791	0.0743
S17	100m S	0.2261	0.4997	0.0163	0.006	0.0071	0.0103	5.253	0.0671	0.6755	0.1313	0.1522
S18	150m S	0.2161	0.4942	0.0174	0.0032	0.0077	0.0107	5.16	0.0661	0.0416	0.1345	0.1437
S19	200m S	0.4943	0.4229	0.0485	0.047	0.0655	0.1102	44.04	0.3339	0.3558	0.8272	0.1594
S20	250m S	0.2025	0.2333	0.0192	0.0168	0.0158	0.0221	14.76	0.1621	0.0604	0.2306	0.1006
S21	300m S	0.0415	0.3166	0.0093	0.0286	0.0372	0.0568	25.83	0.2712	0.2357	0.1667	0.1624
S22	350m S	0.3621	0.8927	0.0345	0.0178	0.0296	0.0447	23.95	0.3761	0.075	0.1581	0.0074
S23	400m S	0.2813	0.1855	0.0304	0.0345	0.0437	0.0634	31.74	0.2668	0.1682	0.4187	0.0484
S24	450m S	0.0053	0.2314	0.0107	0.029	0.0333	0.084	23.78	0.4423	0.2289	0.5904	0.0592
S25	50m W	0.6229	0.1656	0.05	0.014	0.0148	0.0158	11.7	0.0808	0.0017	0.0911	0.2402
S26	100m W	0.0006	0.0572	0.0009	0.0095	0.0069	0.0035	2.665	0.0333	0.1474	0.0743	0.1965

S27	150m W	0.003	0.1048	0.0045	0.009	0.0121	0.008	5.302	0.0716	0.1872	0.2197	0.1242
S28	200m W	0.0008	0.0606	0.0037	0.0098	0.0099	0.0053	2.892	0.0491	0.3846	0.0372	0.154
S29	250m W	0.0018	0.0557	0.0001	0.0109	0.0092	0.0042	2.942	0.04	0.7639	0.0456	0.1165
S30	300m W	0.0181	0.0662	0.0008	0.0062	0.0083	0.0049	2.233	0.0295	0.6136	0.1769	0.1831
S31	350m W	0.0026	0.0514	0.001	0.0124	0.0089	0.0143	1.993	0.0259	0.3868	0.0677	0.0586
S32	400m W	0.0021	0.0523	0.0013	0.011	0.0067	0.0026	2.11	0.0279	0.3336	0.2274	0.0931
S33	450m W	0.0012	0.0597	0.0017	0.0096	0.0095	0.0038	3.522	0.0382	0.7363	0.2669	0.1124
S34	500m w	0.0025	0.0686	0.0011	0.0098	0.0104	0.0042	3.466	0.0361	0.2142	0.4765	0.1945
S35	550m w	0.1597	0.1306	0.0147	0.0167	0.0257	0.0132	10.07	0.0894	1.163	0.1521	0.1297
S36	600m W	0.3411	0.1205	0.0275	0.014	0.0229	0.0105	8.804	0.0575	0.1917	0.0262	0.17
S37	650m W	0.0984	0.1205	0.0096	0.0156	0.0234	0.0087	8.34	0.0853	0.3323	0.106	0.1237
S38	700m W	0.0062	0.0824	0.0007	0.0119	0.0117	0.0053	4.528	0.0459	0.0516	0.053	0.167
S39	750m W	0.1565	0.1044	0.013	0.0114	0.0296	0.011	11	0.1065	0.6607	0.3516	0.1405
S40	800m W	0.0067	0.0931	0.0021	0.0101	0.0116	0.004	3.845	0.0406	0.2243	0.4118	0.1417

S41	850m W	0.0022	0.0907	0.0004	0.0113	0.0094	0.037	2.338	0.0395	0.3732	0.1517	0.1611
S42	900m W	0.0024	0.0643	0.0003	0.0094	0.0131	0.0039	3.24	0.037	0.2025	0.3768	0.1048
S43	950m W	0.0009	0.0665	0.0005	0.01	0.0118	0.0056	3.933	0.0314	0.4199	0.4715	0.133
S44	1000m W	0.0052	0.0878	0.0002	0.0117	0.0134	0.0061	5.538	0.0424	0.5035	0.121	0.1818
S45	1050m W	0.0038	0.0716	0.0006	0.0102	0.0104	0.006	3.319	0.0368	0.196	0.516	0.1392
S46	1100m W	0.0013	0.0683	0.0029	0.0093	0.0106	0.0044	3.499	0.0359	0.0769	0.073	0.1539
S47	1150m W	0	0.0766	0.0003	0.0095	0.0127	0.0057	4.887	0.0383	0.441	0.1619	0.1748
S48	1197.5m W	0	0.0425	0.0009	0.0078	0.0054	0.005	1.896	0.0255	0.192	0.1995	0.1559
Minimum	0		0.0425	0.0001	0.0032	0.0054	0.0026	1.74	0.0255	0.0017	0.0262	0.0012
Maximum	0.6229		0.8927	0.0676	0.0677	0.0807	0.1412	51.96	0.9353	1.163	0.8272	0.2677
Mean	0.112039		0.19714	0.01315	0.01835	0.02365	0.02914	14.0189	0.16609	0.31627	0.27839	0.1145

*: Direction and distance from the thermal spring.

4.2.2 Rocks

4.2.2.1 Petrographic analysis

The geology of the study area comprises of the basaltic rocks of the Karoo lavas. However, outcrops of these rocks are rare in the area; they are covered by deposits of the Kalahari beds. Five representative rock samples were collected from the patchy outcropped of the basaltic rocks in the vicinity of the thermal spring for petrographic analysis.

In the hand specimen the basalt appears greenish grey with white and green amygdules. The white amygdules are more prevalent than the green amygdules.

In thin section the analysed samples of the basalt show amygdaloidal texture with variable sizes of amygdules (Fig. 22). The size of the amygdules varies up to 2 mm. The predominant white amygdules in the hand specimen turned out to be filled by zeolites with generally course grain size (see Fig. 22 A, C, E - F). In local places the vesicles are visible in the basalt (Fig. 22B) and display variable sizes. This indicates that the basalt initially had a vesicular texture which resulted from high gas content released during the deposition of the basalt.

The petrographic investigation of representative thin sections shows that the basalt is essentially made up of fine lath-shaped plagioclase and fine anhedral clinopyroxene crystals associated with considerable amount of opaque minerals (see Fig. 23). The grain size of the plagioclase and pyroxenes are mostly less than 0.5 mm as can be seen in Figure 23. The volume percentage of the plagioclase in the basalt is quite variable ranging between 70% and 45% (see Fig. 23A & E). Moreover, the grain size of the plagioclase crystals are locally variable as can be seen in Figure 23C. In some samples the amount of clinopyroxene exceeds that of plagioclase as can be observed in Figure 23B and E. This indicates that the basalt has variable modal composition. The modal content of the opaque minerals vary between 5 and 10%. Othopyroxene and amphibole occur in trace amounts.

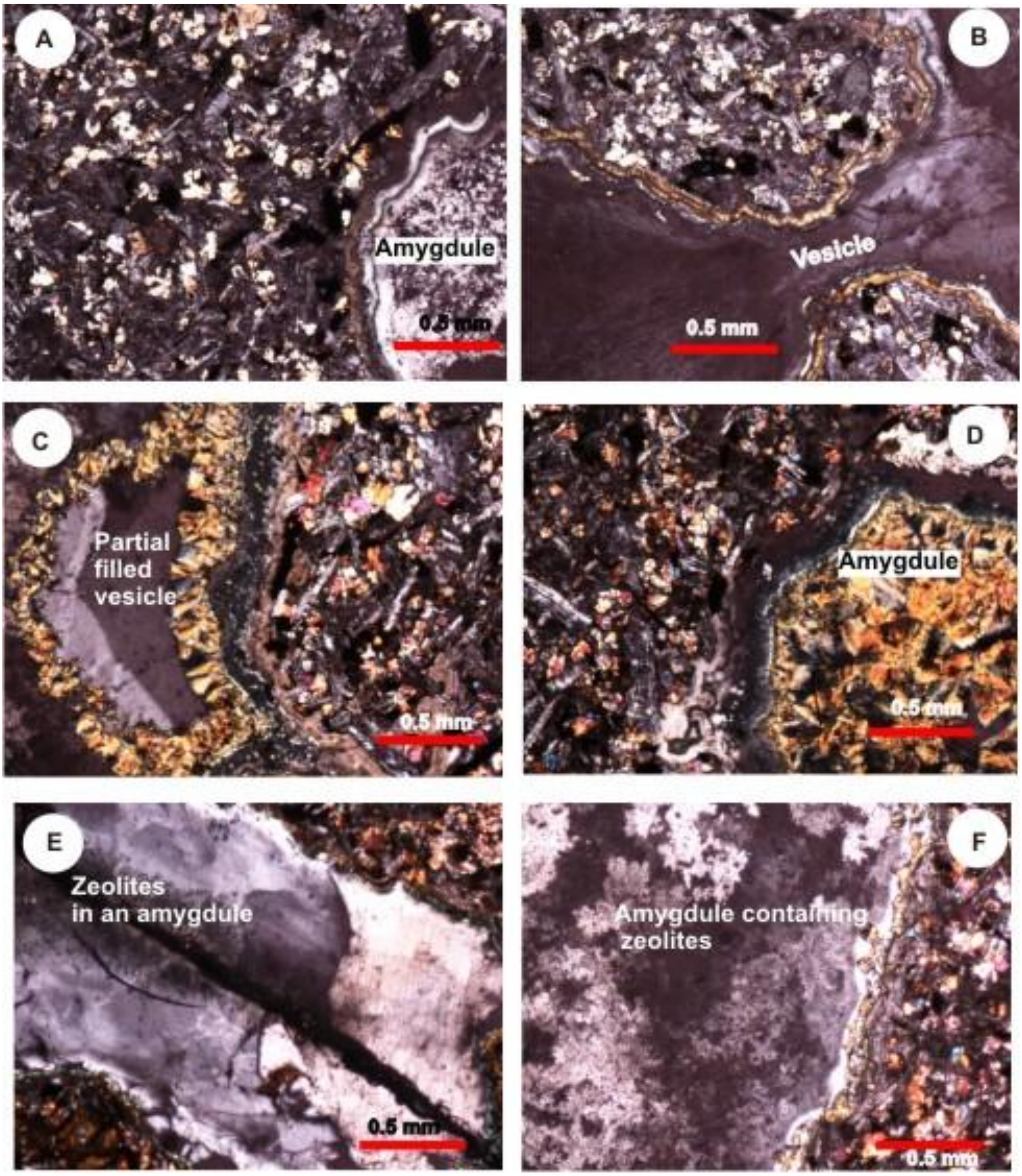


Figure 22. Microphotographs of the basalt showing amygdules (A, C - F) and vesicles (B) as observed under the microscope.

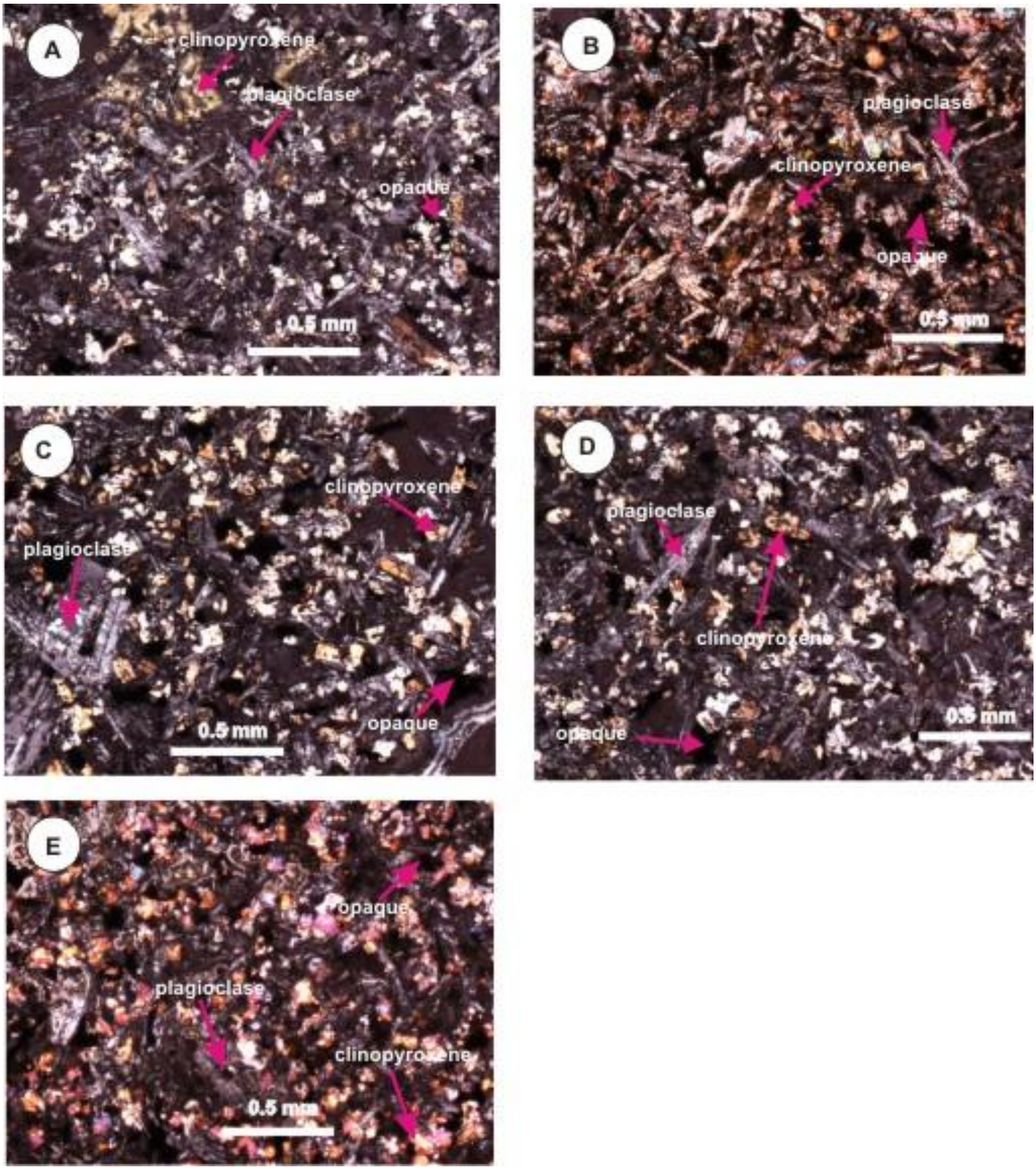


Figure 23. Microphotographs of the basalt showing the variable modal composition: A, C - D plagioclase rich and B and E clinopyroxene rich.

CHAPTER 5.0 - DISCUSSION

5.1 Physico-chemical Parameters

The spring and the groundwater from the pits north of the spring are slightly alkaline to alkaline, brackish to saline and hard to very hard whereas the groundwater west of the springs, river water and the sewage water are acidic to slightly alkaline (with the exception of sample W11, which is alkaline), fresh (with the exception of sample W12, which is brackish) and soft to hard.

The TDS value of the spring water and all the samples of groundwater from the pits north of the thermal spring show a significant high value of TDS as compared to the groundwater samples from the west of the spring, the sewage and the river waters. This suggests that the thermal spring is not from infiltration of local precipitation or fresh surface water. The source area is of regional rather than local extent.

Water alkalinity and hardness are primarily a function of 1) the geology of the area where the surface water is located and 2) the dissolution of carbon dioxide (CO_2) from the atmosphere. The ions responsible for alkalinity and hardness originate from the dissolution of geological minerals into rain and groundwater.

With the exception of one groundwater samples (W5, 200m N of the spring), all the samples of the groundwater from the pits north of the thermal spring and the thermal spring show a hardness greater than the alkalinity, signifying non-carbonate hardness. The water samples from sewage, river and all the groundwater samples from the pits west of the thermal spring (with the exception of one groundwater samples from the west, W12), however, show a hardness less than the alkalinity; suggesting the hardness of these waters is carbonate hardness.

The non-carbonate hardness nature of the thermal spring and all the groundwater north of the thermal spring also revealed that the origin of the thermal spring and the groundwater north of the thermal spring is not local rather a result of deep water circulation from buried regional structures.

More or less similarities in the TDS and pH values and identical carbonate hardness nature between the river samples and the groundwater samples from the pits west of the thermal spring suggest that the groundwater in the west of the thermal spring have a source similar to the river, which is direct precipitations and/or fresh surface water from rainfall; and the groundwater is the percolation of either or both of these sources.

5.2 Rock-Water Interaction

During weathering and water circulation in rocks and soils, ions are leached out and dissolved in groundwater. The geological formations, water-rock interaction and relative mobility of ions are prime factors influencing the geochemistry of groundwater (Ahmed Nur et al., 2012).

The use of scattered plots for TDS vs Na/ (Na + Ca) and TDS vs. Cl/ (Cl + HCO3) can be used to identify rock-water interaction processes.

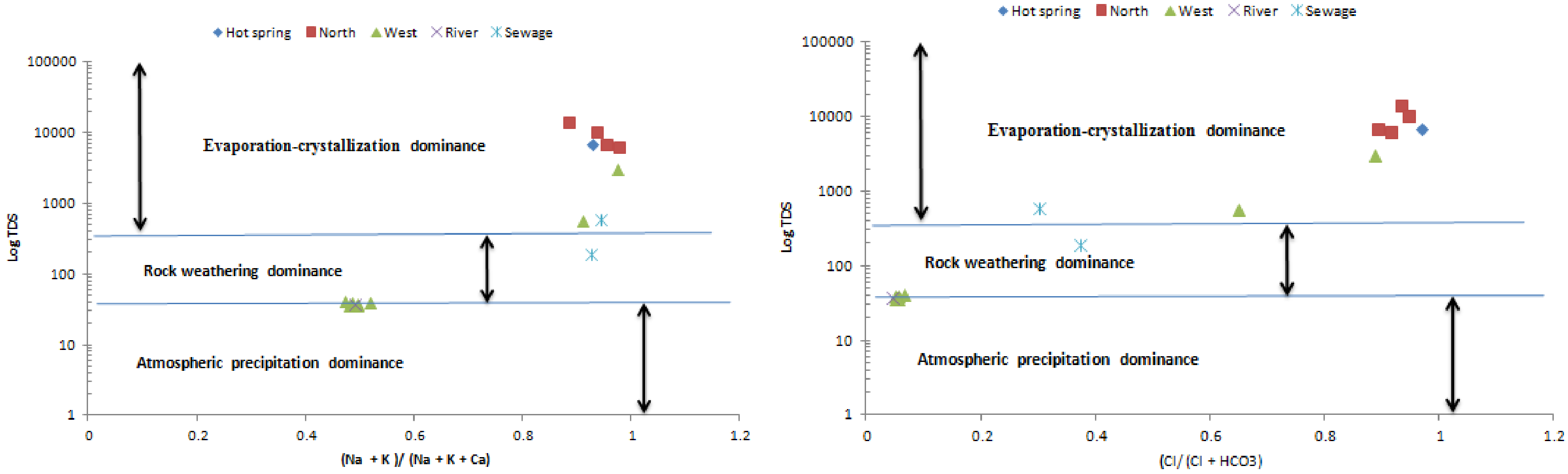


Figure 24. Gibbs diagram for cations and anions in (meq/l).

As shown in the Figure 24, the thermal spring, all the samples of the groundwater from the pits north of the thermal spring and two samples (W11 and W12) of the groundwater from the pits west of thermal spring lie in the region of evaporation – crystallization dominance whereas all the samples of the groundwater from the pits west of the thermal springs (with the exception of sample W11 and W12) and the river water lies on the boundary of rock weathering dominance and atmospheric precipitation dominance signifying the role that both of them they have in the chemistry of the groundwater west of the thermal spring and the river water.

The impact of the rock weathering dominance to the chemistry of groundwater is dependent on the type of rock weathering processes that operate while the groundwater percolate through the different geological formations of the area: precipitation induced chemical weathering along with the dissolution of rock-forming minerals can modify the groundwater chemistry.
To differentiate the rock weathering processes that operate in the area under study the samples were plotted in the Figure 25, Ca + Mg Vs. HCO3 + SO4. As shown in the figure the thermal spring, all the samples of the groundwater from the pits north of the thermal spring and two groundwater samples from the pits west of the thermal spring (W11 and W12) lies below equiline 1:1, indicating silicate weathering is the major weathering process that has influenced the chemistry of the groundwater.

All the samples of the groundwater from the pits west of the thermal spring, with the exception of W11 and W12, and the river water samples, however, fall along the equiline 1:1, indicating that samples have a balanced concentrations of (Ca + Mg) and (HCO3 + SO4). According to Datta & Tyagi (1996) there is an influence of both carbonate and silicate weathering in the chemistry of the water.

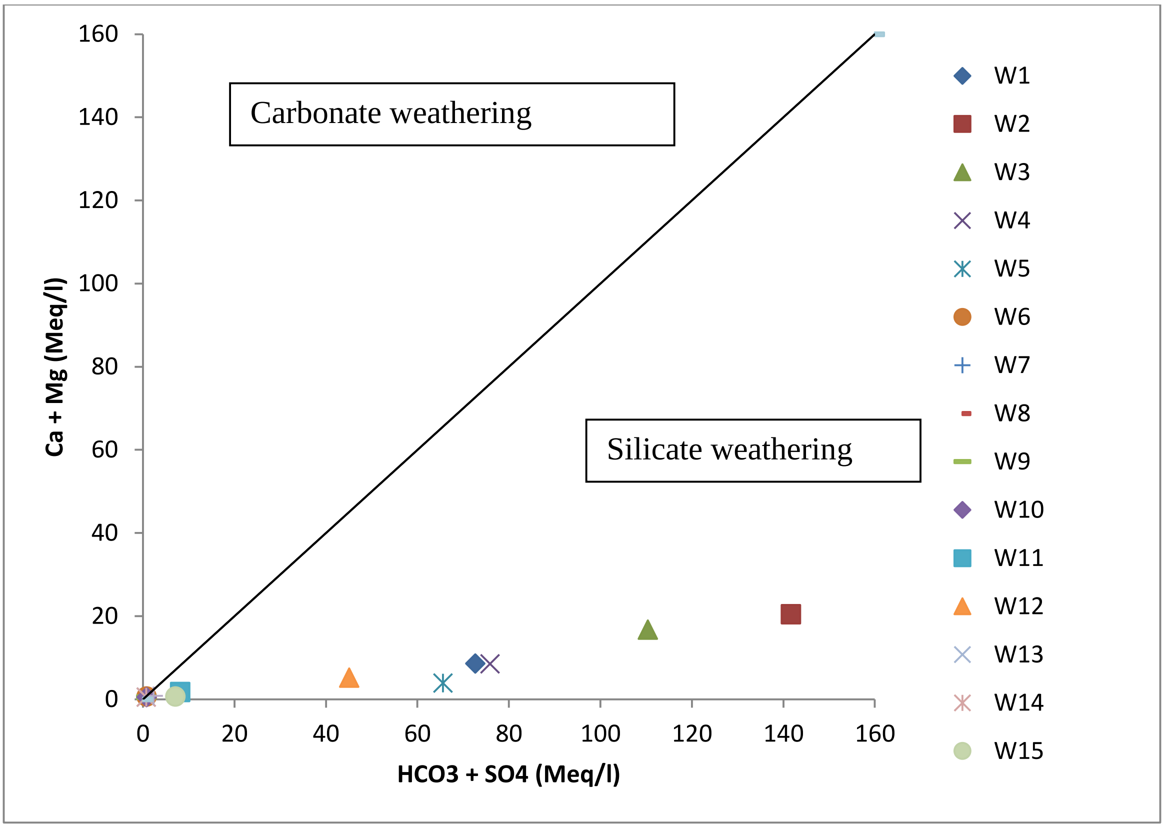


Figure 25. The (Ca + Mg) versus (HCO3 + SO4) scatter diagram for the study area.

5.3 Cations, Anions and Trace elements

From the analysis of the major ions in the water samples, it was observed that Ca^{2+} and Na^{+} are the dominant cations, with the exception of sample W12, which is from west of the thermal spring, where the concentration Mg^{2+} is greater than that of the concentration of Ca^{2+}. In the thermal spring and in all the analyzed samples north of the thermal spring Na^{+} is the dominant cation followed by Ca^{2+} and Mg^{2+} whereas in all the samples west of the thermal spring Ca^{2+} is the dominant cation followed by Na^{+} and Mg^{2+}. In sample W12 Na^{+} is followed by Mg^{2+} and Ca^{2+}. The concentrations of both K^{+} and Li^{+} in the thermal spring and all the groundwater samples from the pits north of the thermal spring are greater than the concentrations in all the other samples.

Hem (1959) stated that calcium is an essential constituent of many igneous-rock minerals, especially of the chain silicates, pyroxene and amphibole, and the feldspars and that calcium also occurs in other silicate minerals which are produced high metamorphism. Some calcium is, therefore, to be expected in water which has been in contact with igneous and metamorphic rock.

A Ca^{2+}/Mg^{2+} molar ratio in water samples that is equal to one indicates dissolution of dolomite rocks, while a greater ratio may represent a more dominant calcite contribution from the rocks. A Ca^{2+}/Mg^{2+} ratio, greater than 2 represents the dissolution of silicate minerals into the groundwater (Tahoora et al., 2014). The thermal spring sample and all the groundwater samples from the pits north of the thermal spring have a Ca^{2+}/Mg^{2+} ratio greater than 2, which indicated the dissolution of silicate minerals into the groundwater. The abundance of Ca^{2+} and Mg^{2+} in the thermal spring and all the groundwater samples from the pits north of the thermal spring could be related to the presence of basaltic rocks in the area in which silicate minerals are the dominant minerals in the rocks. Weathering of these minerals might have contributed Ca^{2+} and Mg^{2+} to the spring and groundwater (Eq. 3 to 5). The thin section study of the rocks from the studied area indicated that plagioclase and pyroxenes are the two dominant minerals in the rock. The weathering of plagioclase, pyroxene and biotite minerals could be represented in the following reactions; equations (3) to (5) in natural systems:

$CaAlSi_2O_8$ (plagioclase [anorthite]) + $2CO_2 + 3H_2O \rightarrow$ Clay minerals (e.g. kaolinite) + Ca^{2+} + $2HCO_3^-$ (3)

$2CaMgFeAl_2Si_3O_{12}$ (pyroxene) + $8CO_2 + 0.5)2 + 11H_2O \rightarrow$ 2Clay minerals (e.g. kaolinite) + $2Fe(OH)_3 + 2Ca^{2+} + 2Mg^{2+} + 8HCO_3^- + 2SiO_2$ (4)

$2K(Mg2Fe2+)AlSiO10(OH)2$ (biotite) + $10CO_2 + 0.5O_2 + 8H_2O \rightarrow$ 2clay minerals (e.g. kaolinite) + $2Fe(OH)_3 + 2K^+ + 4Mg^{2+} + 10HCO_3^- + 4SiO_2$ (5)

With the exception of two samples, all the groundwater samples from the pits west of the thermal spring had A Ca^{2+}/Mg^{2+} ratio between 1 and 2, which indicated the dissolution of calcite. One of the groundwater samples from the pits west of the thermal spring had a Ca^{2+}/Mg^{2+} ratio higher than 2 indicating the dissolution of silicate minerals. This sample is the one nearest to the thermal spring as compared to the others. The other groundwater sample from the pits west of the thermal spring had a Ca^{2+}/Mg^{2+} ratio less than one. The river sample reflects the same value to that of the groundwater samples from the pits west of the thermal spring.

With the exception of one sample, Ca^{2+}/Mg^{2+} ratio values of groundwater samples from the pits west of the thermal spring are slightly higher than river water; suggesting that the groundwater is recent and does not have long residence time within the rocks of the area. This slight increment of Ca^{2+}/Mg^{2+} ratio values in the groundwater is due to more dominant calcite contribution from the dissolution of plagioclase minerals in the rocks of the study area as it was explained above in the form of reaction (Eq. 3)

Table 13. The Calcium (Ca)/Magnesium (Mg) ratio of the water samples

Type/Direction*	Ca	Mg	Ca/Mg ratio	Rock weathering processes
Thermal spring	151.74	12.94	11.73	Dissolution of silicate minerals
50m N	349.8	36.22	9.66	Dissolution of silicate minerals
100m N	294.81	24.92	11.83	Dissolution of silicate minerals
150m N	154.82	9.989	15.50	Dissolution of silicate minerals
200m N	67.34	6.756	9.97	Dissolution of silicate minerals
300m W	7.287	3.483	2.09	Dissolution of silicate minerals
350m W	5.812	3.208	1.81	More dominant calcite contribution
400m W	5.554	3.085	1.80	More dominant calcite contribution
500m W	5.484	3.119	1.76	More dominant calcite contribution
550m W	5.633	3.116	1.81	More dominant calcite contribution
750m W	18.886	9.677	1.95	More dominant calcite contribution
1050m W	36.04	41.72	0.86	Dissolution of dolomite rocks
1197.5m W	5.346	3.106	1.72	More dominant calcite contribution
River random	5.45	3.187	1.71	More dominant calcite contribution
Sewage 1	8.523	2.791	3.05	Dissolution of silicate minerals
Sewage 2	5.01	6.58	0.76	Dissolution of dolomite rocks

*: Direction and distance from the thermal spring.

The trend of concentrations of Na^+ and K^+ ions in all the analyzed samples are different from that of Ca^{2+} and Mg^{2+}. In the thermal springs and in all the samples of the groundwater from the pits north of the thermal spring the concentrations of Na^+ and K^+ ions are much higher than the concentration of Ca^{2+} and Mg^{2+} ions: suggesting that the dissolution of plagioclase and pyroxene minerals is not the only source of these elevated values of Na^+ and K^+ ions in these water. In all the samples of groundwater from the pits west of the thermal spring and river water, the concentrations of Na^+ and K^+ ions shows the same trend to that of the concentrations of Ca^{2+} and Mg^{2+} in these water. The elevated concentrations of Na^+ and K^+ ions in the thermal springs and in all the samples of the groundwater from the pits north of the thermal spring signifying more supplements of the deep fluids that have deep origin.

The general dominance of anions in the thermal spring and all the groundwater samples from the pits north of the thermal spring were in the order of $Cl^- > SO_4^{2-} > HCO_3^- > Br^- > F^- > CO_3^{2-} > NO_3^-$. In all the samples west of the thermal springs and the river water the dominant anion is bicarbonates with chloride being subdominant, followed by sulphate : $HCO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-} > NO_3^- > F^{--} > Br^- > NO_2^-$. This is with an exception to two samples (sample W11 and W12). In the two samples sulphate is the dominant anion with chloride being subdominant, followed by bicarbonate: $SO_4^{2-} > Cl^- > HCO_3^- > CO_3^{2--} > NO_3^- > Br^- > F^-$.

Cl^- and SO_4^{2-} as are not the major constituents in the minerals of basaltic rocks. The dominancy of Cl^- and SO_4^{2-} in the thermal spring and in all the samples of the groundwater from the pits north of the thermal spring suggesting more supplements of the deep fluids that have deep origin.

With exception of sewage water, PO_4^{3-} is absent in all the analysed water samples. In sewage water its concentration reaches up to 88.1 mg/l. NO_2^- are absent in the thermal spring, in all the groundwater samples from the pits north of the thermal springs, in the river water sample and in sewage samples. In the samples of the groundwater from the pits west of the thermal spring NO_2^- exist only in the samples W6, W7, W9, W10 and W13 only having minor concentration. In the remaining samples is NO_2^- absent. With the exception of one of the sewage sample ($NO_3^- = 20.23$ mg/l), NO_3^- is found having a minor concentration in all the analyzed water samples. The high concentrations of PO_4^{3-} and NO_3^-- in the sewage water are mainly attributed to sewage effluents. Nitrogen compounds (ammonium salts, nitrites and nitrates, etc.) found in urban water bodies are mainly due to decomposition of proteinous compounds which enter with sewage. In the thermal spring and in all the samples of groundwater from the pits north of the thermal spring bromide exist having a significant concentration whereas in all the samples of groundwater from the pits west of the thermal spring, river samples and sewage samples the concentrations of bromide is minor. The existence of bromide having such concentrations in the thermal spring and in all the samples of the groundwater from pits north of the thermal spring is attributed to the supplements of the deep fluids that have deep origin.

The analyzed cations and anions in both sediments and water samples more or less show the same trend of dominancy but vary in magnitude of concentration. In the sediments samples the dominant cations are Na^+, Ca^{2+} and K^+ and the dominant anions are Cl^- and SO_4^{2-}. Such compositional nature of the sediments suggests that the source of the cations and anions for the water is not linked to the composition of the sediments rather to the different processes and origin describe above.

The analyzed trace elements in both the sediments and water samples more or less exhibit the same trend of dominancy but vary in magnitude of concentrations. The concentration of each analyzed trace element is greater in sediment than in the water with the exception of the concentration of Ni: the concentration of Ni in the water samples is greater than the concentration of Ni in the sediments.

The concentration of Ni is high in the thermal spring and the groundwater from the pits north of the thermal spring followed by the sewage water and then the groundwater samples from the pits west of the thermal spring and the river samples.

The abundance of Ni in igneous rocks generally correlates with those of Mg, Cr and Co. Even though the bed rocks are basaltic rocks, this general truth is not applicable in the case of the study area. Ni concentration is much higher than the concentration of Cr and Co. The mean concentration of Ni in the thermal spring and the groundwater samples from the pits north of the hot spring is 1.754 mg/l. The mean concentration of Ni for the groundwater samples from the pits west of the thermal springs and river water sample is 0.529 mg/l whereas from the sewage samples the mean is 0.795 mg/l. The high concentration of Ni in the groundwater west of the thermal springs, river water and sewage is both by silicate weathering, sewage itself and leachate from the waste. The high concentration of Ni in the thermal spring and in the groundwater from the thermal spring is related deep seated origin of the fluid or magmatic fluids.

All the remaining analysed trace elements in the groundwater from pits west of the thermal springs, sewage and river could be derived from precipitation dissolution of minerals.

Generally, the analysed trace elements in the thermal spring and in the groundwater samples from the pits north of the thermal spring have origin from fluids of deep origin.

All the analysed trace elements, in the sediments from samples west, east, south of the thermal spring are could be derived from silicate weathering. The iron (Fe) concentration in the sediment is much higher than its concentration in the water samples. Since clay minerals carry more iron than sand grains, this element is principally associated with silt-clay fraction.

CHAPTER 6 – WATER SUITABILITY

6.1 General

The analysed cations, anions and trace elements of the thermal spring water and all the samples of groundwater from the pits north and west of the thermal spring were compared and evaluated with respect to the drinking water standards set by Botswana Bureau of Standards (BOBS) (2009) and World Health Organisation (WHO), (2003 third edition) (Table 14). The WHO standard is important in the event of bottling the water for the international market or for consumption by overseas visitors.

The thermal spring, all the samples of groundwater from the pits north and west of the thermal spring satisfy the pH drinking water standard of both WHO and Botswana Bureau of Standards.

With the exception of the sample W12, all the samples of groundwater from pits west of the thermal spring suit the EC and TDS standard of both WHO and Botswana Bureau of Standards whereas sample W12, thermal spring water and all the samples of groundwater from the pits north of the thermal spring is highly above the recommended limits of standards set by both WHO and Botswana Bureau of Standards.

All analysed cations and anions in all the samples of groundwater from pits west of the thermal spring, except sample W12, satisfy the standard of both WHO and Botswana Bureau of Standards. Because of the existing concentration of Na^+, Cl^-, Br^- and $SO4^{2-}$, sample W12, thermal spring water and all the samples of groundwater from the pits north of the thermal spring do not satisfy the standard of both WHO and Botswana Bureau of Standards.

The analysed thermal spring water and all the samples of groundwater from the pits north and west of the thermal spring don't satisfy the standard of both WHO and Botswana Bureau of Standards because of the existing concentration of Ni and Pb in the waters.

Table 14. Drinking water standards by WHO and BOBS

	BOBS	WHO
EC (µS/cm)	1500-3100	1500
pH	5-10	6.5-9.5

TDS (mg/l)	1000-2000	
Ca (mg/l)	150-200	
K (mg/l)	50-100	
Na (mg/l)	200-400	200
Mg (mg/l)	70-100	
Cl (mg/l)	200-600	250
F (mg/l)	1-1.5	1.5
NO_3 (mg/l)	50	50
NO_2 (mg/l)	3	3
SO_4^{2-}(mg/l)	250-400	500
Zn (mg/l)	5-10	
As (mg/l)	0.01	0.01
Cd (mg/l)	0.003	0.003
Cr (mg/l)	0.05	0.05
Co (mg/l)	0.5-1	
Cu (mg/l)	2	2
Fe (mg/l)	0.3-2	
Pb (mg/l)	0.01	0.01
Mn (mg/l)	0.1-0.5	0.4
Ni (mg/l)	0.07	0.02
Ba (mg/l)	0.7	0.7

CHAPTER 7- CONCLUSION AND RECOMMENDATION

7.1 Conclusion

The hydrogeochemistry of any source of water is an important aspect to know in order to address matters such as contamination and quality. In the analysed water samples generally based on the mean values of the chemical parameters, the cations were in the order of abundance as $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Li^+$ and the anions were in the order of abundance as $Cl^- > SO_4^{2-} > HCO_3^- > PO_4^{3-} > Br^- > CO_3^{2-} > NO_3^- > F^- > NO_2^-$. In the analysed sediment samples the cations and anions are in the order of $Na^+ > Ca^{2+} > K^+ > Mg^{2+} > Li^+$ and $SO_4^{2-} > Cl^- > NO_3^- > Fl^- > Br^- > NO_2^- > PO_4^{3-}$, respectively.

75 % the analyzed groundwater samples from the pits west of the thermal spring show some similarities in the trend of concentration of the different constituents of the groundwater with the river water, suggesting that the groundwater is recent or derived from precipitation. A slight increment of values in the analyzed major cations, anions, and trace elements in the groundwater of this area is due to the dissolution of different minerals in the rocks of the study area. The remaining 25% the groundwater samples from this part of the study area suggest that precipitation is not the sole source of groundwater and it could be derived from both precipitation and fluids of deep origin.

The thermal spring and the groundwater north of the thermal springs are characterized by higher mineralization, and this could be attributed to the more supplement of the deep fluids that have deep origin. This implies that the source of the spring and the groundwater north of the thermal spring have a regional origin.

The thermal spring water and all groundwater in the studied area are not recommended for drinking purposes.

7.2 Recommendation

Chemical analyses revealed that the thermal spring water and the groundwater in the surrounding of the thermal spring are not safe for drinking purposes. However, the people in the area are currently using the water for different domestic and self-medicating purposes including drinking. The responsible health offices in the area should take this result into account and consider sensitizing the public on the hazardous effect of the water. Other options such as treatment of the water as well as limitation of access to the water should be taken into consideration.

CHAPTER 8- REFERENCES

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APPENDICES

Sampling Positions for water samples

Sample ID	Sample Type, Location and Direction*	GPS coordinates
W1	Thermal spring	S 17°47`27.7116" E 25°11`53.3436"
W2	GW 50m N	S 17°47`26.8692" E 25°11`54.0348"
W3	GW 100m N	S 17°47`25.944" E 25°11`55.6188"
W4	GW 150m N	S 17°47`24.63" E 25°11`56.7744"
W5	GW 200m N	S 17°47`23.6436" E 25°11`58.1136"
W6	GW 300m W	S 17°47`19.212" E 25°11`45.996"
W7	GW 350m W	S 17°47`18.4092" E 25°11`43.9764"
W8	GW 400m W	S 17°47`17.3292" E 25°11`41.8776"
W9	GW 500m W	S 17°47`16.5984" E 25°11`39.93"
W10	GW 550m W	S 17°47`15.9504" E 25°11`39.0228"
W11	GW 750m W	S 17°47`16.7748" E 25°11`30.4008"
W12	GW 1050m W	S 17°47`16.0728" E 25°11`20.058"
W13	GW 1197.5m W	S 17°47`8.3616" E 25°11`18.1396"
W14	River	
W15	Sewage 1	S 17°48`4.9392" E 25°10`57.6732"
W16	Sewage 2	S 17°48`5.4432" E 25°11`1.1724"