# Investigating Recharge Rates in Table Mountain Springs Using Oxygen and Hydrogen Isotopes

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# ABSTRACT

This thesis investigates the monthly variation in hydrogen and oxygen isotope composition of four springs at the foot of Table Mountain, and by comparing this variation with that of local rainfall, estimates are made of their recharge rate. The oxygen, hydrogen, and EC data for Main spring, De Waal spring, Albion spring, and Newlands springs for the years 2013 to 2016 are presented. The oxygen and hydrogen isotope composition of monthly rainfall collected nearby at the University of Cape Town (UCT) over the same period are also presented. The rainfall data ranges in δD and $\delta^{18}O$ values from -57 to +18 ‰ and -8.1 to +3.19 ‰, respectively, with most δD and $\delta^{18}O$ values between -60 and -20‰, and -10 and +4‰. The data shows seasonal pattern, with lower δD and $\delta^{18}O$ values in winter and higher in summer. The UCT monthly rainfall samples define a meteoric water line whose equation is $\delta D = 6.03*\delta^{18}O + 7.07$, which is similar to previous versions of the equation from the 1995 to 2008 data. The range of recorded EC values for the springs are distinct, the average EC values for each of the spring is; Albion spring 207 µS/cm, Newlands spring 128 µS/cm, Main spring 171 µS/cm and De Waal spring 166 µS/cm. The isotope compositions of the springs are also well grouped, with each spring plotting in a distinct field on a δD and $\delta^{18}O$ plot. Main spring has the lowest δD and $\delta^{18}O$ values and De Waal spring has the highest δD and $\delta^{18}O$ values. The springs' average δD and $\delta^{18}O$ values for the three years sampled are -7.7 and -2.74‰ (Albion), -6.48 and -2.46‰ (De Waal), -11.52 and -3.48‰ (Main) and -8.49 and -3.14‰ (Newlands).

The d-excess of the rainfall range between -11.56 and +33.12 and for the springs is between 0.17 and 27.97. The summer months (low rainfall) have lower d-excess values than the winter months (higher rainfall). There is a positive relationship between the rainfall d-excess, springs d-excess and the rainfall amount, as the amount of rainfall increases the d-excess values of both the rainfall and springs increase. The change in the springs d-excess values clearly mimics that of the rainfall. The similar pattern changes of the d-excess values and δD and $\delta^{18}O$ of the rainfall is reflected in the spring water, suggesting that recharge is occurring rather rapidly and from the d-excess values, the recovery seem to occur for some springs from month to month. De Waal spring mimics the rainfall d-excess very closely, the changes are almost at the same time, and therefore the De Waal spring is recharged the fastest, recovery occurs from month to month. Newlands d-excess does not change at the same time at the rainfall's d-excess, Newlands is the slowest spring to recover, with recharge occurring at least within three months. Main spring and Albion spring fall in between the fastest and slowest recovering spring. The springs are recharged at different rates but with the general average of recharge rate of one to three months of recovery.

The difference in δD and $\delta^{18}O$ values between the springs is best explained in terms of difference in average altitude of the potential recharge areas. Average altitude of potential recharge estimated from the topographic map is as follows: Albion spring 286 m, Newlands spring 359 m, Main Spring 518 m and for the De Waal spring 335 m. There is a strong negative correlation between δD and average altitude (r = -0.90) and for $\delta^{18}O$ and average altitude (r = -0.82). In 2012 the annual weighted mean $\delta^{18}O$ value of rainfall on top of Table Mountain was -4.0 ‰, therefore De Waal spring ($\delta^{18}O$ -2.46 ‰) has a small component of mountain rainfall compared to Main spring ($\delta^{18}O$ -3.48 ‰), with Albion spring and Newlands spring in between.

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# Abbreviations, Acronyms and Units

**CTMP2010 -** Cape Town Millipore Water
**EC -** Electrical Conductivity
**EMMA -** End-Member Mixing Analysis
**GMWL -** Global Meteoric Water Line
**IAEA -** International Atomic Energy Agency
**LMWL -** Local Meteoric Water Line
**MAMSL**- Meters above Sea Level
**MWL -** Meteoric Water Line
**OSGW -** Original Slope Groundwater
**RMW -** Water and Rocky Mountain Water
**RMA -** Reduced Major Axis Regression
**SGW -** Slope Groundwater
**SAB -** South African Breweries
**SAWS -** South African weather services
**SAWS -** South African Weather Service
**SLAP -** Standard Light Antarctic Precipitation
**SMOW -** Standard Mean Ocean Water SMOW
**TCT -** Taoyuan-Chungli Tableland
**UCT -** University of Cape Town
**V-SMOW -** Vienna standard mean ocean water

**$\delta D$ -** hydrogen isotope
**$\delta^{18}O$ -** oxygen isotope
**% -** percentage
**ºC -** degrees Celsius
**Ga -** billion years
**km -** kilometre
**$km_2$ -** square kilometre
**mS/M -** millisiemens/meter
**mg/L -** milligrams per liter
**Ma -** million years
**mm -** millimetre
**mg** – milligram
**µS/cm** – microsiemens
**T** – temperature
**l/min** – liter per minute
**l/day** – liter per day

**D-excess -** deuterium excess
**$CO_2$ -** carbon dioxide
**$N_2$ -** nitrogen
**$H_2$ -** hydrogen
**$H_2O$ -** water
**$H_3$ -** tritium
**r -** Correlation coefficient

# Chapter 1 Introduction

## 1.1 Overview

The need to increase our knowledge on groundwater systems is becoming vital, as the volume of surface fresh water is increasingly unable to sustain the water demand. Groundwater is becoming a more viable source as a substitute for surface fresh water to meet the water demand. Groundwater is water that is underneath the Earth's surface in pore space between soil particles, rocks and in fractured rocks. The water-bearing rocks and unconsolidated materials are called aquifers and are recharged by precipitation infiltrating into the subsurface. The water accumulates in large quantities in underground layers of open spaces, from which water can be extracted. Groundwater can also flow to the surface naturally, discharge can occur as seeps, springs or groundwater flowing in or recharging wetlands and rivers. The use of groundwater for drinking, agriculture and other general purposes is likely to increase in the future hence an increased interest in understanding the recharge rate of groundwater is required. In this study, the focus will be on springs in fractured rocks and mountain slope scree. The water flows naturally to the surface and occurs as springs at the foot of Table Mountain. The recharge rate is an important process of groundwater management. This could help for future use of the springs' water, as when the recharge rate of the springs is known, a sustainable use of the springs' water will be practiced to avoid over extraction and deplete the natural resource. The main aim of the study is to determine at what rate the springs are recharged by the groundwater.

### 1.1.1 Springs on the Lower Slope of Table Mountain

Historically the springs have been an important source of water, firstly for the indigenous people who lived in the area and later for the European settlers. The first thing the settlers did was to construct furrows to connect the springs on the lower slope of the mountain to supply water for the people in the settlement (now Cape Town) and visiting ships (Timoney, 1993). The people mostly used the water for irrigation, to supply visiting ships with fresh produce (food). The minor furrows were later upgraded to underground and wider canals (Murray, 2008). The canals and springs were used to serve people in Cape Town, and the city's canal system was also created by the Dutch settlers as a fire and irrigation system in the mid- to the late 1600s (Cape Times, 2010; Capetrail, 2013). The Main spring which is a part of the current study was one of the important sources of water; pipes were laid from Main spring in the centre of Cape Town, now known as Oranjezicht suburb (Timoney, 1993). Due to the increase in population and during the hot seasons, the town experienced water shortage. It was proposed that reservoirs should be constructed to eliminate this problem. Every available spring on the lower slope was piped to this reservoir which was later named the Molteno (Timoney, 1993; Murray, 2008). Later on more reservoirs were constructed; a pipeline would usually be constructed from a spring to the new reservoir. Some of these canals are still accessible today. There are about 6.5 km of underground canals that carry storm water and spring water from the Table Mountain into the Atlantic Ocean (Cape Times, 2010). Due to the outbreak of bubonic plague, some were covered by the British, and the remaining canals were filled and covered by 1903 (Cape Times, 2010; Capetrail, 2013).

The springs can serve as an important reserve of water for future use. They should be a part of the City of Cape Town water supply plan; this makes the flow rate and the recharge rate of the springs important. The lower slope of the Table Mountain has got a lot of perennial springs, but some time ago it was decided to choose only four to study continuously for this study. The current use of the water from these springs is as follows: The Main spring in Oranjezicht, which produces over 3.5 million liters of water per day (Cape Town partnership, 2012), is used to irrigate the Green Point Urban Park. There is a pipeline running from the Main spring in Belmont Avenue (Oranjezicht), to the Green Point Urban Park. The De Waal spring flows into the reservoir in De Waal Park, situated between Orange and Hof Street (Hilton, 2010). The Newlands spring is used commercially, the spring is abstracted by SAB (South African Breweries), and all beer from the Newlands Brewery is made from the spring water, no municipal water used (Porter, 2012). The water is not chemically treated in any way before is used for beer production. The overflow of this spring is directed into the Liesbeek River, at the end of Spring Street in Newlands. The spring is owned by SAB, and has been for well over 100 years (Porter, 2012). Some of the water from the springs in Newlands is used to irrigate local schools grounds. Albion Spring in the past had been flowing unused into the Liesbeek River and now is linked to the city's water supplement water, occasionally pumped to a reservoir (Armstrong, 2014). The spring flowing into the river helps sustain the river's flow, particularly in summer. The water is firstly treated and then integrated into the city's water supply plan. The drinking quality of the water is very good. The water is treated with chlorine. Chlorine in water acts as a disinfectant, killing bacteria's and viruses that grow in water supply reservoirs.

### 1.1.2 Stable Isotopes in the Hydrological Cycle

The main purpose of this section is to give a broad picture of the hydrological cycle and the stable isotopes system in the hydrological cycle. Mook (2001) wrote, "The hydrosphere can be characterised as a system of different reservoirs from which water, solutes, and energy are exchanged by the hydrological cycle.'' The hydrological cycle starts with evaporation from the oceans, then rainfall precipitation (meteoric water) fall over the ocean and over the continents. This precipitation returns to the ocean via rivers, groundwater seepage, and melting glacial, while the rest is recycled back to the atmosphere by re-evaporation. (Figure 1) shows the hydrologic cycle, and that the oxygen and hydrogen isotopes are integral parts of the natural water molecules that fall as rain or snow (Davila-Olmo, 2011). They are transported through the different stages of the hydrologic cycle. Gat (1996) wrote that change in the isotopic composition of water within the water cycle provides a distinctive signature, relating such water to the different phases of the cycle.

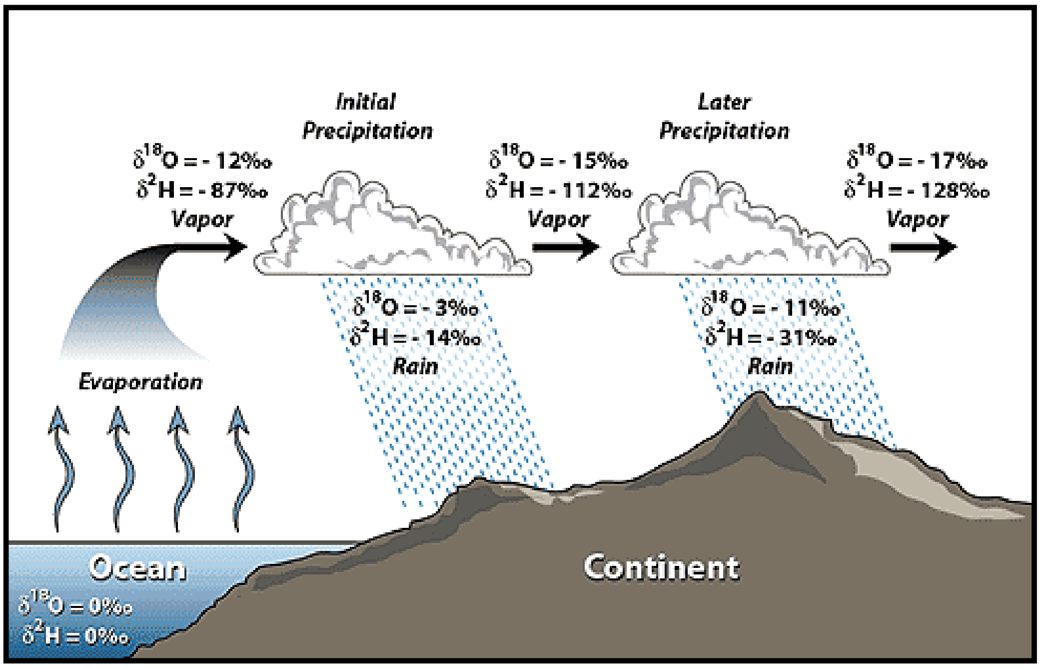


**Figure 1. Stable isotopes compositions in the hydrological cycle, isotopic compositions of hydrogen and oxygen are different within the different components of the hydrologic cycle. Rainout effect on $\delta D$ and $\delta^{18}O$, diagram from SAHRA (2017) based on Hoefs (1997) and Coplen et al. (2000) work.**

Isotopes are atoms of the same element that have different numbers of neutrons but the same number of protons. Differences in the number of neutrons among the various isotopes of an element mean that the various isotopes have different masses, oxygen occurs as three stable isotopes in nature the oxygen isotopes (oxygen-16, oxygen-17, and oxygen-18) and the hydrogen as two isotopes (protium and deuterium) (Mook, 2001). These mass differences are large enough for many physical, chemical, and biological processes or reactions to fractionate or change the relative proportions of different isotopes of the same element in various compounds (Kendall & McDonnell, 1998; Gat, 1996). Because of fractionation process water develop a specific isotopic composition (ratio of heavy to light isotopes) in the different phases of the hydrological cycle. This distinctive isotopic composition can serve as tracers for precipitation and groundwater (Clark & Fritz, 1997; Kummar et al. 2010). Stable isotopes of oxygen and hydrogen in the hydrological cycle can, therefore, be used as tracers. Davila-Olmo (2011) wrote, “as a tracer isotopic compositions of water can be used as a method of characterising and quantifying the effect of different flow contributing sources to different water bodies.’’ The stable isotopes compositions will be used in this study to track groundwater movement, the isotopic compositions of the rainfall and the water from the springs will be compared to try and find correlations between the two water bodies. The primary aim is to see when or if ever the isotopic composition of the rainfall is reflected in the water that comes out of springs, consequently providing information on the recharge rate of the springs at the slope of Table Mountain.

As mentioned above because of fractionation process water develops a specific isotopic composition, a specific geographical area can develop a distinctive local precipitation composition for that area. Dansgaard (1964) discussed the factors which influence the isotope composition of precipitation in a specific area. These factors are; the latitude effect, continental effect, altitude effect, temperature effect and amount effect. The influence of the different factors affect the isotopic composition in the following manner; with increasing in latitude, increasing distance from the coast, an increase altitude and increasing amount of rainfall, the isotopic composition of the precipitation becomes depleted in $\delta D$ and $\delta^{18}O$. The temperature effect differs with a specific geographical area, in

Cape Town the correlation between isotope values and temperature is poor; nevertheless Harris et al. (2010) noted that there is a general tendency for the months with the colder average temperature to have precipitation with lighter isotopic composition, with the winter months receiving more rainfall than the summer months.

- The latitude effect - As most moisture is sourced from the tropical oceans, the moisture tends to flow towards the poles from the mid- or high latitude ocean areas. As the moisture moves further away from the tropics, the isotopic composition changes. Condensation and rainout favours the removal of the heavier isotopes and so the precipitation at higher latitude has more negative $\delta D$ and $\delta^{18}O$ values. High latitude rainfall is depleted of isotope values compared to low latitude rainfall.

- The continental effect - Rainout is the main causes of increasingly negative isotope values for precipitation that is further inland. The isotope value in the clouds gets depleted as the amount of moisture remaining gets smaller. This is due to both the rainout effect and the further away the clouds get from the source of the moisture.

- The altitude effect - The altitude effect is caused mainly by rainfall that is triggered by orographic uplift. The heavy isotope content of the rainfall decreases with increasing altitude. Rainfall at higher elevations will have less distance to travel to the ground and less chance for evaporative enrichment, in which the lighter isotopes evaporate.

- The amount effect - The amount effect, large rainstorms have lower heavy isotope content. When there is an increase of rainfall amount in one location, the isotopic signature becomes lighter.

- The temperature effect - With increase temperature, rainfall becomes enriched in the heavier isotopes. The changes in temperature results in seasonal isotope variation, during the winter months the rainfall has lower heavy isotopes and during the summer months, the rainfall has got higher heavy isotopes. This applies specifically to an area with a Mediterranean climate, with winter months receiving more rainfall than summer months.

**Table 1. Summary of five major factors that may influence the isotope composition of the rainfall.**

| **Five major factors** | **Results of the effects** |
|---|---|
| The continental effect | The further inland the precipitation is from the source (ocean) of the moisture, the lower $\delta D$ and $\delta^{18}O$ |
| The latitude effect | The higher latitude has lower $\delta D$ and $\delta^{18}O$ |
| The altitude effect | The higher the elevation of recharge, the lighter the $\delta D$ and $\delta^{18}O$ |
| The amount effect | The higher the rainfall, the lighter the $\delta D$ and $\delta^{18}O$ |
| The temperature effect | The lower the temperature, the lighter the $\delta D$ and $\delta^{18}O$ |

### 1.1.3 Meteoric Water Line

Craig (1961) produced a global scale correlation of $\delta D$ and $\delta^{18}O$ of fresh water based on a large dataset and the values correspond to a line best-fit (Figure 2), which is known as the Global Meteoric Water Line (GMWL) defined by the following equation: $\delta D= 8*\delta^{18}O + 10$. The Meteoric Water Line is produced by an equation that depicts the relation between hydrogen and oxygen isotopes ratios of the world's meteoric water. A set of data can be used to calculate line of best fit (local meteoric water line), for a given area, the samples of precipitation will plot along a local meteoric water line (LMWL). This correlation defines the trend of the local meteoric water line. The GMWL is the cumulative result of lots of LMWLs for regions of a different climate. As moisture air move from the tropics to the poles, the data along the GMWL is influenced by meteorological processes, such as the amount of water vapour and temperature, but mostly influenced by a rainout of atmospheric moisture (Gat, 1996). The result from the rainout enhances the removal of heavy isotopes by increasing isotope fractionation factors. This shift in the isotopic composition is evident on the GMWL.

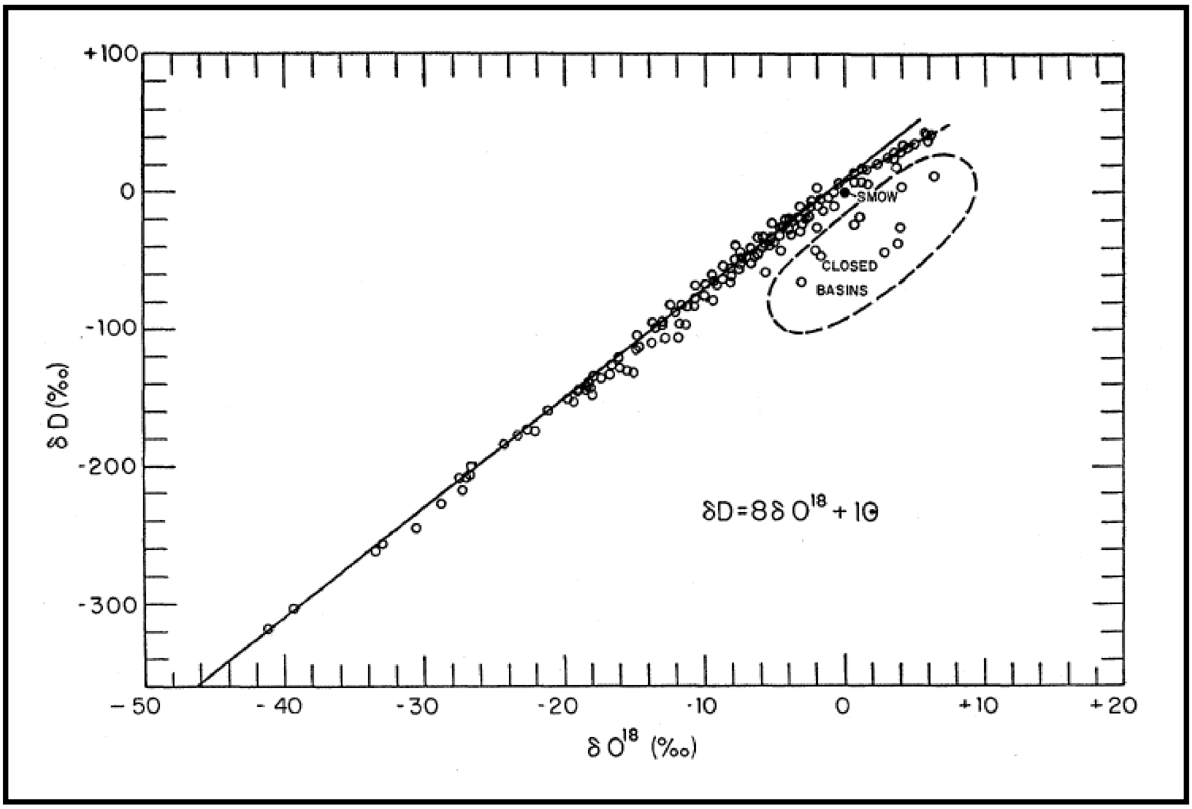


**Figure 2. The graph depicts the relationship between hydrogen and oxygen stable isotopes in precipitation. The equation that describes this relationship is called the Global Meteoric Water Line (GMWL), diagram from Craig (1961).**

### 1.1.4 Deuterium Excess

Shifts away from the best fit line (GMWL) can be expressed by a parameter known as the deuterium excess or commonly known as d-excess (Dansgaard, 1964). The deuterium excess is calculated for a sample of known δD and $\delta^{18}$O values by the equation: d-excess = δD – $\delta^{18}$O. The δD and $\delta^{18}$O are the values for the water sample. The d value is a representation of the humidity of the source region. This means the slope along which vapour and residual water plot on a δD – $\delta^{18}$O graph will vary as a result of the degree of exchange or isotopic equilibrium. Evaporation under lower relative humidity regions will generate lines with lower slopes, and the opposite for regions with relatively higher humidity. At a different relative amount of humidity and the resulting water samples will be displaced from the GMWL, the deuterium excess of water samples measures the displacement (Clark & Fritz, 1997). Increased deuterium excess in precipitation can also arise from the significant addition of evaporated moisture from continental basins to the water vapour traveling inland. Deuterium excess can also be used to distinguish different moisture sources that recharge groundwater for example springs.

### 1.1.5 Stable isotope hydrology in Western Cape

The southwestern and southern coastal areas of Southern Africa are covered by the fractured rocks which have a potential to be a major source of groundwater supply. A large quantity of groundwater occurs in the secondary openings in the fractured rocks. The quartzite of the Peninsula Formation in the Table Mountain Group is identified or recognised as an aquifer. This is the Peninsula aquifer, which is the second largest aquifer system in South Africa (Weaver, et al., 1999). The Peninsula Formation spread over the Western Cape and Eastern Cape Provinces varies in thickness, therefore the volume of the aquifer is not easy to determine and other characteristics of the aquifer have not been studied. Stable isotopes of hydrogen and oxygen have been used as an investigation tool to study the aquifer to expand the knowledge and do research on the aquifer, to grasp how the aquifer operates/function. This is to manage the aquifer and develop schemes to use the groundwater sustainably.

In the greater Cape Town area, oxygen and hydrogen stable isotopes were applied as an investigational tool for multiple purposes on the Peninsula aquifer. February et al. (2004) studied the Fynbos vegetation to determine the source of water used by the vegetation growing on the Table Mountain Group soil. The aim of the study was to determine the water source for the Fynbos vegetation and establish if the vegetation depended on the Peninsula Aquifer for permanent water supply. This was to investigate the impact over abstraction of groundwater from the aquifer will have on the Fynbos vegetation. The study concluded that the different Fynbos species depended on groundwater from different depth (level) within the soils; therefore different water table will affect the different species differently. Stable isotopes were also used to assess the problems of urban hydrology in the city. Harries et al. (1999) applied stable isotopes to evaluate the potential use of oxygen and hydrogen as tracers of the origin of groundwater. Water samples were collected from various sources (locations) around Cape Town, from the water treatment plants, boreholes, and springs. This study concluded groundwater from the borehole located on the Cape-Flats is isotopically different from the spring-water of the lower slope of Table Mountain, indicating different sources (different aquifers).

Stable isotopes have also been used to investigate the Peninsula Aquifer outside the greater Cape Town area, as the aquifer host rock (Peninsula Formation) is vast and extends over two provinces. Casework was conducted in the Kammamassie area which is located in the east section of the Klein Karoo, this area consists of the Peninsula Aquifer and Nardown Formations Aquifers (Table Mountain Group Aquifer systems). Wu (2005) used oxygen and hydrogen stable isotopes, among other tools to estimate the groundwater recharge rate in the area. Groundwater from boreholes, springs' and a river in the area were sampled and the study revealed, the recharge rate obtained was lower than initially expected and the groundwater was recharged by a source from a higher elevation (mountain zone). Work was also carried in the Agter-Witzenberg valley, Cave' et al. (2002) used oxygen and hydrogen stable isotopes to develop a conceptual groundwater flow model. The stable isotopes and geochemistry were used to trace groundwater recharge and flow pattern for the aquifers in the area (Table Mountain Group Aquifers). The isotope data shows groundwater recharge both by rainfall in the mountain zone and by surface drainage systems in the valley.

## 1.2 Aim of project

### 1.2.1 Previous studies on the four springs

This project was initiated to compare the monthly variations in isotopic composition of rainfall; collected at UCT, with the vitiations of the springs' water. The study focuses on four springs, two in the southern suburbs (Albion spring and Newlands spring) and two more in the city center (De Waal spring and Main spring). There has been little research done on the specific four springs investigated in this study. In the past, data has been sporadically collected from 1996 to 2008 and a paper was published reporting the results; in this paper Harris et al. (2010), determined the oxygen and hydrogen isotope composition of rainfall collected over the time at University of Cape Town (UCT).

The difference in isotope composition of rainfall was detectable in the isotope composition of water collected from springs and suggests that the groundwater is recharged by approximately 50% within three years. Only from 2013 the data was collected on a regular basis. Honours students from the Department of Geological Sciences did their dissertations work on this study, in 2013, Netshilindzi (2013) sampled 17 springs around the Table Mountain (

Figure 3), bridal spring was a part of this study but is not shown on the figure (Harris personal communication, 2017). The springs were sampled twice that year once during the summer season and again during the winter season. The following year in 2014 only 4 springs were sampled and they were sampled on a monthly bases, Zondi (2014) reported that each of the 4 springs have a distinct isotopic signature and there is little overlap between the data for the springs, despite the distance between some springs being less than 1 km in some cases. This indicates that the zones of recharge are different with differences in the average elevation of the recharge areas. The students were also comparing the monthly variation in rainfall composition with that of the springs in order to establish the rate of recharge of the springs. Malatji (2015) worked on a dataset from 2014-2015 and she reported that all the springs were recharged by both the rainfall from both 2014 and 2015 as recharge is continuous and concluded that the springs are rapidly recharged on a minimum of fewer than two months to approximately a year. The isotopic values of the springs also reflect the following, during dry summer with low rainfall the isotope values reflected high $\delta D$ and $\delta^{18}O$ values and during the wet winter reflected lower $\delta D$ and $\delta^{18}O$ values.

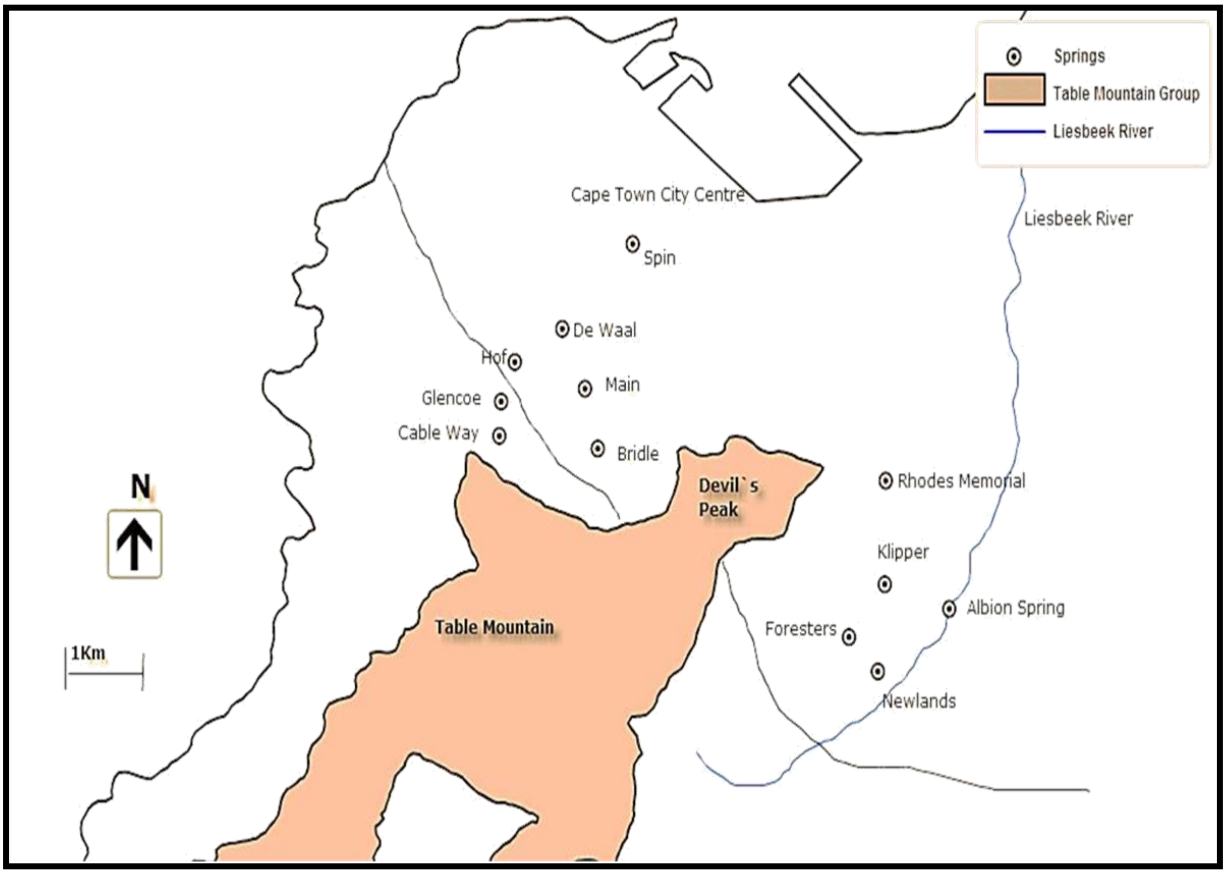


**Figure 3. Location map of the springs sampled in 2013, map from Harris et al. (2000).**

### 1.2.2 Hypotheses

Initially, three hypotheses about recharge of springs were considered. These were made on the basis of the limited evidence at the start of the project.

- The source of water recharging the springs, as rainfall can either percolate into the subsurface to recharge the Peninsula Aquifer or infiltrate the slope scree to recharge the alluvium Aquifer. It was initially thought that water from Peninsula aquifer recharged the springs.
- Because the springs are thought to be recharged by the same source, it was assumed that the isotopic composition of the springs will be the same or fall within the same compositional range.
- The electrical conductivity (EC) values of the four springs were also predicted to be approximately the same.

### 1.2.3 Main Research Question

From previous research work, questions became evident and in order to address the main research question for this study, these questions and recommendations will be addressed from previous work. The main research question of this study is what is the estimated rate of recharge of the springs? To solve this problem some of the following questions have to be addressed.

- Are the springs recharged by the Peninsula Aquifer or the alluvium Aquifer on the lower slope of the mountain? Part of the study will be to investigate the occurrence of a shallow mountain alluvium aquifer.
- What is the flow pattern of the water discharged at the springs? Previous work has shown that the springs are compositionally slightly different.
- Albion spring has got much higher EC readings than the rest of the springs, what is the possible reason for the higher EC values? Investigate any compositional differences.
- What is the recharge rate of the springs; the springs' isotope signature and the rainfall isotope signature will be compared to determine the recharge rate?

### 1.2.4 Objectives of the Thesis

The main aim is to determine the rate of recharge of groundwater in the aquifer that supplies the springs. In order to do this, the temporal variation in isotope composition would be compared to the variation in isotope composition of rain collected at UCT. In determining the recharge rate, the origin and flow-path of the recharge water will be investigated and the nature of the aquifer. The oxygen and hydrogen characterisations can be used to determine the flow paths that water follows from the time precipitation hits the ground until discharge at the outlet springs (McDonnell and Kendall, 1998; Davila-Olma, 2011). Oxygen and hydrogen isotopes will be used as tracers to determine the rate at which water flows from the point of recharge (rainfall) to the point of discharge (springs). Mook (2001) wrote that, "Natural isotopes can be used as tracers to follow elements of the water in their natural course." Previous work on the Table Mountain springs had focused on short-term trends (one-year data); this study will investigate the long-term trends of the dataset.

## 1.3 International and national previous work on stable isotopes hydrology

Change of isotopic composition in water; from groundwater, surface water, and atmospheric water have been studied on both a local and global scale. There have been relatively few published studies of the Cape Town area. However, research from other countries has been reviewed below. This literature review will focus on four aspects: (a) how stable isotopes have been used to identify different sources of water (b) how stable isotopes have been used as tracers (c) what are possible causes of different electrical conductivity (EC), EC is a proxy for dissolved salts/constituents in groundwater in general and (d) studies on long-term variability in the isotope composition of spring water elsewhere.

### 1.3.1 Stable isotopes used to identify different water bodies sources

Groundwater can have more than one source, precipitation (rainfall) or surface water. Springs and seepage points can also be recharged by multiple sources, aquifers from different formations, whether be a shallow aquifer near the surface or an aquifer at a lower depth. Stable isotopes can be used as a tool to identify the different sources of water in a study area. Once below the water table, the water's isotopic composition remains unchanged unless it mixes with isotopically different waters. This signature reflects the water's history and origin before infiltration, hence it can be used to interpret the process by which recharge occurs. Peng et al. (2010) outlined the advantages of using stable isotopes to identify the different water sources; firstly hydrogen and oxygen isotopes are compositions of the water molecule, and secondly, unique hydrogen and oxygen isotopic signatures can be differentiated from waters in various environments due to related isotopic fractionation effects.

In 2014 Bryant and Blake (2014) reported that springs located on the lower slope of Table Mountain were recharged by water from the Peninsula Formation aquifer. But Diamond (2015) concluded that the water recharging the springs might come from a shallow aquifer, water in the alluvium on the Table Mountain slope. One of the differences between the Peninsula Formation Aquifer and the alluvium Aquifer is, groundwater in the shallow depths is able to discharge at a spring or other outlet within weeks or months, whilst groundwater at deeper depths flow more slowly and sustain steady discharge for years. If the springs are been replenished by water from the alluvium Aquifer and not the Peninsula Formation Aquifer, this should be evident in the chemical and the isotope composition, and if both the aquifers replenish the springs, the springs' water should initial reflect the isotopic composition of the alluvium Aquifer and subsequently the isotopic composition of the Peninsula Formation Aquifer. When it rains in the Table Mountain area, the rainfall can either infiltrate into the subsurface (Peninsula Formation) and the Peninsula Formation Aquifer is recharged, and the water can also flow as surface water and later infiltrate the alluvium, therefore, recharge the alluvium Aquifer of the slopes Table Mountain, and there is also an altitude difference between the Peninsula Formation Aquifer and the alluvium Aquifer.

Mazor and Verhagen (1983) studied sixteen thermal springs across South Africa to determine the source of water recharging the springs, if the springs were recharged by different water bodies. The aim was to see if the springs were recharged by both the meteoric water and rivers adjacent to the springs, both the springs, and the rivers were sampled. The study shows that all the thermal springs water studied were of the meteoric origin. In the Witwatersrand basin, the water some of the deep gold mines situated in the area was analysed using trace element concentrations, strontium isotopic composition, oxygen, and hydrogen stable isotopes. Duane et al. (1997) sampled twelve mines to determine the origin and isotopic evolution of the brines and for comparison with brines from other Precambrian areas. The oxygen and hydrogen isotopes reveal a pattern that classifies the samples as meteoric but with modifications. The modifications were due to surface infiltration and deep mining conditions (humidity). Mountainous landscapes are especially important as groundwater recharge zones, as mountain areas receive more rainfall than plains. In Taiwan, oxygen and hydrogen stable isotopic composition of water and hydrochemical information were applied to quantify contribution ratios of different sources of groundwater. The Peng et al. (2010) was able to verify the source and significance of the original slope groundwater (OSGW) for a creeping slope next to a hydropower plant, by using stable isotopes. This investigation was initiated as excess slope groundwater (SGW) could lead to slope failure after a heavy rainfall event. Water $\delta D$ and $\delta^{18}O$ values showed that local precipitation and OSGW are two end members for slope groundwater of the studied creep slope.

Peng et al. (2012) also used hydrogen and oxygen stable isotopes and radioactive tritium isotopes to assess groundwater sources in the Taoyuan-Chungli Tableland (TCT), north-western Taiwan. Identification of groundwater sources was important for properly managing water resource in the area. This study area also had copious ponds distributed throughout, which were excavated to store water for agriculture. Water samples including precipitation, pond water, stream water, and groundwater all collected for isotopic composition determination. The results of the investigation indicate that both precipitation and pond water were the end sources of proximal shallow groundwater in the TCT. In central Japan, work was carried out in the Ashio Mountains and the Kanto plain. Liu & Yamanaka (2012) clearly identified recharge sources and their corresponding contributions to the sustainable management of aquifers to ensure that the needs of humans and ecosystems were met. Groundwater recharge in mountain-plain transitional areas could generally be divided into direct recharge of local precipitation and mountain-front recharge. Isotope and hydrochemistry analysis indicate that direct infiltration by precipitation, Watarase River seepage and mountain block recharge were the three main recharge sources in the study area (Liu & Yamanaka, 2012). The isotopic signatures of water from the Watarase River and local precipitation could be clearly distinguished. Furthermore, he also demonstrated that end-member mixing analysis (EMMA) using stable isotope and chloride tracers were used for estimation of the contribution ration of different recharge sources with a notably low error. All the examples above are relevant to the study because results from previous work done the four springs, each spring had its own specific isotope composition signature. The examples show how stable isotopes have been used to identify different water sources occurring in a study area.

### 1.3.2 The use of stable isotopes as tracers

There are many benefits of using stable oxygen and hydrogen isotopes as natural tracers. Peng et al. (2014) wrote that firstly they are highly conservative; since the major constituents of water are oxygen and hydrogen, and because they can be used to identify and provide new insight into groundwater recharge on a regional and local scale. The isotope ratios in water do not easily change, except where there is a huge amount of evaporation and/or mixing with of water of different isotope ratio. The isotopic tracer property is used in this study as an investigation tool. A great deal of work has been done both nationally and internationally and on a local and regional scale using isotopic tracers as an investigative tool. This tool has been used in hydrogeology field to monitor groundwater movement, $\delta D$ and $\delta^{18}O$ isotopes are used in studies in mine hydrology, urban hydrology, weathering processes, and movement of water in soil (Mook, 2001). There is a growing concern with groundwater quality degrading through over-abstraction, contamination, and climate change.

The contamination can vary from toxin or pollutant contamination, and a growing movement to use more of it as drinking water. Stable isotopes of the water molecule (δD and $\delta^{18}O$) have been studied in aquifers around the world to investigate these concerns. The following two examples are studies (local and international) were isotope tracers were used as an investigative tool to monitor the effect of water abstraction.

A local case study is on the Table Mountain Group Aquifer (Peninsula Formation Aquifer) and plant ecology reported by (February, et al., 2004). Because many of the endemic plant species are vulnerable to groundwater abstraction, the study attempted to determine the extent to which the plant species relied on a permanent water source fed from the aquifer. Over abstraction can lead to the extinction of certain species, so safe abstraction levels need to be determined. The study focuses on two parts, firstly to determine the hydrogen isotope ratio of the aquifer water, and secondly to relate the isotopic ratio of the water extracted from plants growing in the area. The hydrogen and oxygen isotope analysis of the water extracted from the plant reflected the water sources used by the plant. This study was able to show which plants depended on subsurface water and which plants used water from deeper lying water. Another study where there was a growing concern about over abstraction and stable isotopes tracers were used as an investigation tool is in Andhra Pradesh (India). The Maheshwaram watershed was investigated using stable isotopes of the water for tracing and identify the groundwater recharge and water-use in this typical rural Indian watershed experiencing agricultural water-resource overexploitation (Negrel, et al., 2011). The two cycles of monsoon precipitation were monitored, while at the same time the spatial and temporal variations in δD and $\delta^{18}O$ in the groundwater and the precipitation were measured. The investigation's results showed periods during which evaporation affected groundwater quality, and confirmed that the groundwater most probably comes from present-day precipitation (mostly monsoon precipitation).

There has also been much work done using stable isotopes as tracers to investigate groundwater recharge rate and flow regime of a particular area. A case study where broad a spectrum of environmental tracers (stable isotopes) were employed on a regional scale was in Botswana. The study area is situated on the Eastern fringe of the Kalahari between Serowe and Orapa in the Central District of Botswana. In this case study Stadler et al. (2010) used stable isotope (δD and $\delta^{18}O$) among other isotopes hydrological to analyse recharge conditions, flow regimes and their time scales. The study showed that there was mixing between over and underlying aquifers in the area. The regional-scale groundwater flow regime in the aquifer is slow, and that groundwater is recharged in Serowe and Orapa. In Southern Italy at Mt Vulture, stable isotopes were used to determine the isotopic signature of the groundwater. Paternoster et al. (2008) work was able to determine the isotopic signature of the groundwater and showed that the hydrogeological and structural setting of the area has produced a groundwater system roughly relatively homogenous. Rainwater samples were collected monthly and their isotopic composition (δD and $\delta^{18}O$) was analysed, and at the same time groundwater was sampled from springs and wells throughout the study area. The main purpose of this work was to define a groundwater circulation model able to explain the relationship between the meteoric recharge and the groundwater system. Barth (2000) used stable isotopes as tracers in a study to unravel the evolutionary processes of variably mineralised groundwaters from sedimentary reservoirs of late Paleozoic to Early Mesozoic age in Central Europe (N Switzerland – SW Germany). Groundwater samples were collected from Late Paleozoic (Permian) to Early Mesozoic (Triassiac) sedimentary reservoirs.

The results from this work was able to show that sediment-hosted groundwaters in the study area are influenced by extensive interactions with aquifer rocks (comprising evaporates, sulfates, carbonates, and clays) and that there is a large-scale inter-aquifer mixing. (Figure 4) shows investigated groundwaters along the GMWL, some of the samples fall below the GMWL due to water-rock interaction and/or prolonged groundwater residence times. The investigated springs are assumed to be recharged by the rainfall in the recharge zone. The examples show the useful way stable isotopes can be used as tracers. The stable isotope signature of the rainfall can be monitored to see if or when the water sampled of the springs have the same isotopic signature as the rainfall or when the isotope composition of the springs water have the same trends as the rainfall isotope composition.

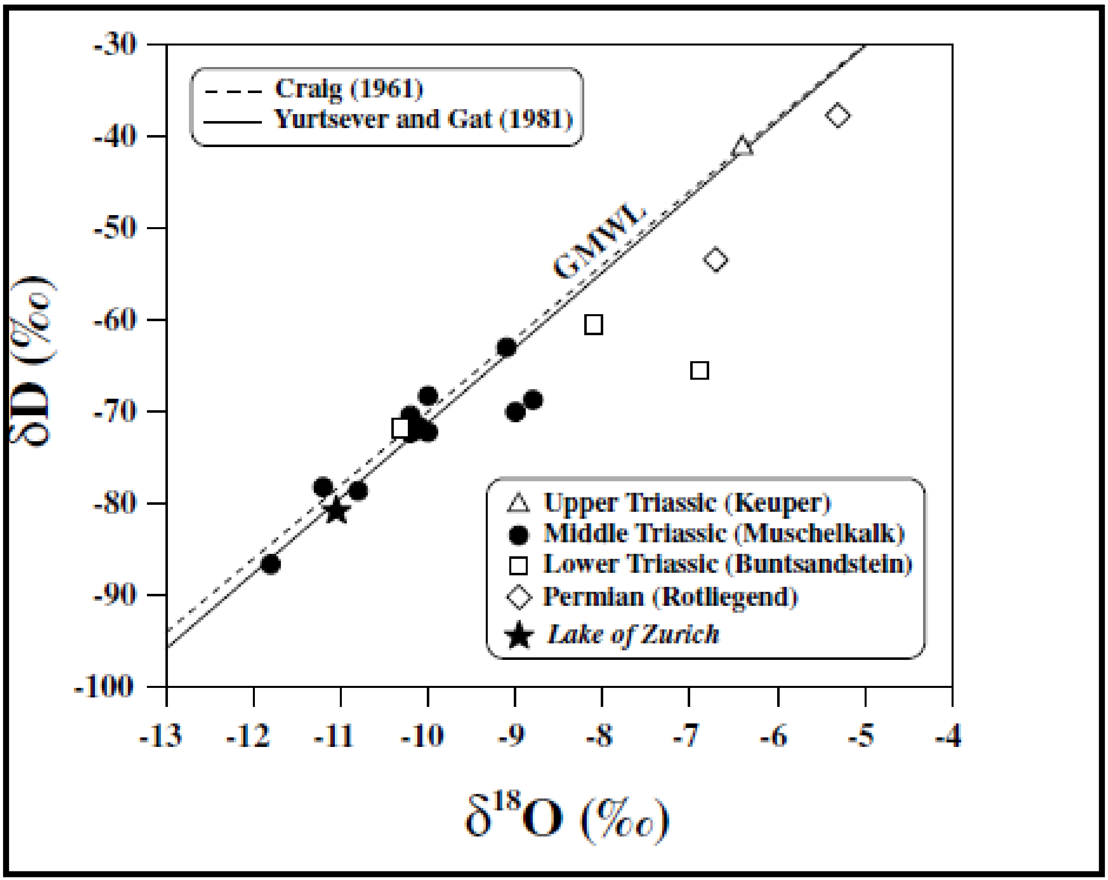


**Figure 4. δD and δ$^{18}$O diagram for sediment-hosted groundwater, diagram from Barth (2000).**

### 1.3.3 Variation in electrical conductivity (EC) values in groundwater.

During field investigation of this project, while collecting water samples, the electrical conductivity (EC) composition of the springs' water was measured. The EC values recorded differ slightly from spring to spring. Electrical conductivity is a proxy for dissolved salts in the water. Song et al. (2006) noted that the EC reflects the total dissolved ion concentrations in water bodies, and to a certain extent, the length of flow paths and residence times underground. Water samples with low EC will have low dissolved salts and the opposite for samples with high EC. Like oxygen and hydrogen isotopes, EC can also be employed as a natural tracer to determine water sources, migration, and water mixing, since EC can differ from water source to water source.

Concentration of dissolved salts in groundwater can differ due to many reasons; the rock-water interaction is one of the reasons, Appelo et al. (1983) wrote the variation may result from different lithologies, although this is not applicable in the Table Mountain Group, the water is usually confined in the quartzite's. This means high EC values for the groundwater could imply that groundwater experiences a greater degree of water-rock interaction than surface water does, this is especially more apparent for deeper aquifer. Deep groundwater experiences more rock-water interaction and is likely to have higher EC values, probably because of the minerals dissolved in the water. Sami (1992) wrote chemical weathering of the aquifer (sedimentary aquifer) contributes little to the total dissolved solids because of the resistant nature of the material. Electrical conductivity can also differ due to man induced difference in the land use (anthropogenic activity), for example, water might flow an area where there are agricultural activities. Furthermore, pollution can also influence the EC of groundwater; EC values in polluted water are higher than non-polluted waters due to higher ion content. The vegetation of a specific area might influence the EC values and rainfall-runoff can change the EC value (Appelo, et al., 1983). Sami (1992) noted a few reasons why a sedimentary aquifer can be saline; the saline can originate from: (a) the sea water intrusion, (b) mixing of rainfall with connate water in the sediment deposited in a marine environment, (c) the amount of dissolved salts near the soil surface during slow diffuse recharge, (d) evaporitic salt deposits leaching by water percolating through preferential pathways and lastly (e) chemical weathering of the aquifer. Example (a) and (b) are not factors in the investigated springs'.

The EC value within a specific study area can differ from one sample point to another, for example, seepage zones, springs, and contributing streams. There are many study cases in the literature were EC values have been investigated and the possible causes for the difference in EC values. The following two study cases shows examples of how lithology affected the EC value of the particular study area. In the Struisbaai area, a case study was initiated to determine the causes of the high salinity water. A sample of town water-supply was collected in June 1990 from a tap at Struibaai Hotel and the EC was found to be 658 mS/m (4150 mg/L of dissolved salts) (Weaver, et al., 1999). Weaver et al. (1999) argued that with the relatively high permeability of calcrete, it is not likely that after 50 000 years the connate seawater is still encountered in sufficient quantities as to be a cause of the high salinities encountered in the area. As the calcretes have some permeability it is highly unlikely that there is sufficient residual connate seawater which could give rise to the salinities encountered in the Struisbaai water-supply. A high-mountain stream in the northern Italian Alps was surveyed for changes in electrical conductivity (EC) along the stream course. The Grossklausenbach is a tributary of the upper Ahr (Aurino) in the northern Italian province of Bozen (Bolzano), the stream flows in a glaciated valley. The EC of water contributing to the stream varies with the lithology drained, permitting a chemical gauging of contributing areas. This EC routing technique method was used and is considered a valuable tool for the recognition of different contribution. Appelo et al. (1983) noted that the sequence of the different geological units was only approximately known, but there was clear evidence that the hydrochemical properties of springs and seepage zones are related to the lithological unit that is drained.

Heavy rainfall (storms) can play a role in the increase of the EC value, in mountainous terrain precipitation is believed to flow due to the steep slopes in combination with the hydrophobic soils until it can enter the subsurface environment (Laudon & Slaymaker, 1997). High EC could also be caused by storm uptake during its contact with the soil surface during runoff. The springs have low EC values, but the Albion spring has higher EC values than the three other springs. Part of the work for this thesis is to determine why the Albion spring has slightly higher EC values. From the examples above shows that the EC of a particular area can be influenced by many factors.

### 1.3.4 Studies on long-term variability in the isotope composition of spring water

The results from prior work done at the four springs have shown that each spring has a distinct isotopic composition signature and there is little overlap between the dataset for the different springs. There are many factors that could cause this difference, one being a possible mixing of different aquifers. Water from a shallow aquifer closer to the surface might mix with water from an aquifer that layer at deeper depths, or aquifers from different rock formation water mixing. Another possible factor is the altitude, at Database River in the Ashio Mountains and the Kanto Plain (Liu & Yamanaka, 2012) was able to show the obvious altitude effect in and around the study area, there were several tributaries to the Watarase within the study area that originate in mountains with elevations that range from 223 to 681 meters above sea level. The isotopic signatures revealed an obvious altitude effect. This work was able to show a close relationship between the isotope values of the river and the elevation of the catchment corresponding to each sampling point. Low $\delta$D and $\delta^{18}$O values of the river water were due to the high elevation of the recharge area (zone). He was also able to calculate the mean residence times of river water and groundwater. As for the four springs investigated in this study Zondi (2014) previously concluded that the variation in the average isotopic compositions of the springs could be explained by the elevation at which recharge occurs, she said this was the consequence of the elevation of recharge, as the higher the altitude of recharge the longer it will take the rain water to reach the springs. Her investigation was on a short term (one-year data); this thesis will look at the data on a long-term basis, to verify her conclusion.

## 1.4 Limitation of the study

Only from 2013 was the springs' isotopic composition changes monitored on a regular (monthly) basis. This study aims to look and present long-term changes evident from the data. Currently the project has been on-going for 4 years but extending the project to 10 years will enable us to monitor the timing of major shifts in the springs' compositions relative to that of the rainfall, and therefore determine the rate of recharge. But unfortunately, the length of the time of monitoring could be a limitation; this needs to be evaluated maybe the key is in the length of the time of the monitoring.

# Chapter 2 spring sites description

The Cape Peninsula (Figure 5) is a ~470 $Km_2$ area of varied topography and varied weather. This chapter will outline the site location, geology of the area, hydrogeology (aquifers), and the climate of the region, with a focus on the rainfall and temperature.

## 2.1 Site location

The study area is located in Cape Town a coastal city in the Western Cape Province in South Africa see (Figure 5). The area is bounded by Table Mountain on the one side and the Cape Flats on the other, situated along the northern and eastern parts of the lower slope of Table Mountain. Table Mountain is characterised by vertical, high cliffs with a flat top, with Devil's Peak and Lion Head on either side of the mountain. The mountain stands at 1086 mamsl at the highest point and then gradually changes into the gentle lower slope at the foot of the mountain. The site location base solid geology is dominated by the sedimentary rocks of the Table Mountain Group, which overlie the basement Malmesbury Group and Cape Granite Suite (Geological-Survey, 1984). The lower slopes are often covered with sandstone debris which gives rise to Mountain scree.

The four springs investigated, two are located in the city center and the other two in the southern suburbs. Cape Town's city center is on the northern edge of the city. The area was chosen as the springs appear at the foot of Table Mountain and the spring's water was easily accessible to sample. By springs I am referring to a location where groundwater naturally seeps (emerges) from the subsurface to the surface of the earth, the investigated springs in this project are all perennial springs. The four springs sampled are situated on the lower slope of the mountain; the GPS coordinates in (Table 2). Main spring and De Waal spring are located just south of the city center (Cape Town), and Newlands spring and Albion spring are located in the Southern suburbs area. Main spring is situated in Oranjezicht suburb; the spring is located just north of the Oranjezicht city urban farm. The De Waal Spring is also located in Oranjezicht suburb, the spring is located north of the De Waal Park in the Molteno reservoir, the spring flows into the reservoir. The Albion spring is located in the Rondebosch suburb, near the Liesbeek River. Albion Spring flows into the Liesbeek River and can be seen when looking towards the mountain while standing on the footbridge over the river in Kingbury Park, behind Albion close. Newlands spring is located in the Newlands Suburb on Springs Street, at the end of the Cul de sac. The over flow spring water can be seen gushing out of a PVC pipe at the end of the road.

**Table 2. The GPS coordinates of the springs' location, elevation, and yields.**

| Sites | Latitude | Longitude | Elevation (mamsl) | Yields (l/day) |
|---|---|---|---|---|
| Main Spring | 33°56'30.79''S | 18°24'55.25''E | 115 | $2.2x10^6$ |
| De Waal Spring | 33°56'3.92''S | 18°24'43.94''E | 60 | $1.4x10^6$ |
| Albion Spring | 33°58'1.58''S | 18°28'4.26''E | 20 | $3.0x10^6$ |
| Newlands Spring | 33°58'27.88''S | 18°27'27.93''E | 40 | $1.55x10^6$ |

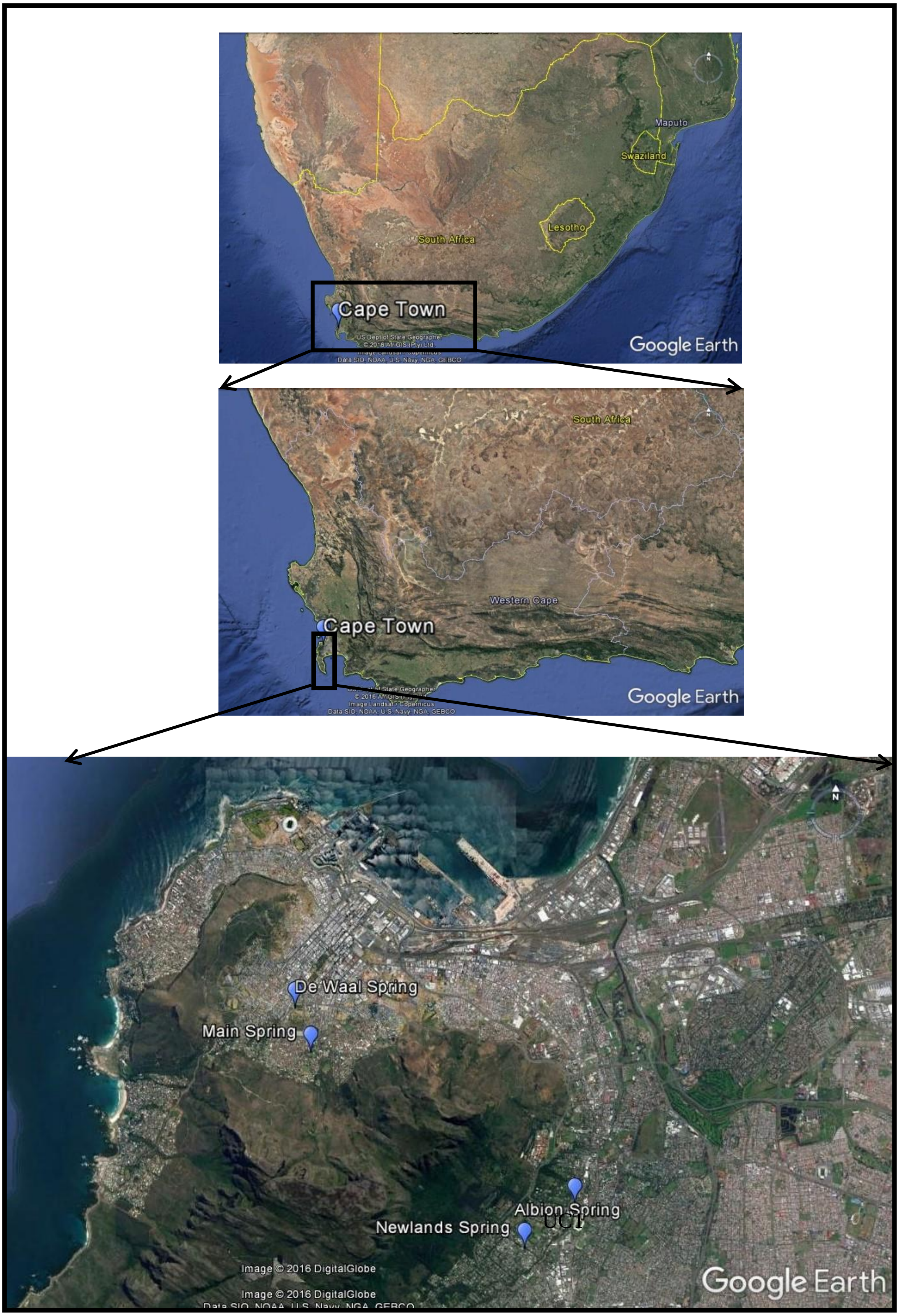


**Figure 5. Location map of the investigated springs, map created google earth.**

## 2.2 Geology

### 2.2.1 Introduction

The Geology of South Africa covers a long and complex geological evolution which dates back to ~3600 Ma years ago. The focus for this section will be on the geology of Cape Town metropolitan area and surrounding areas. The study area geology is dominated by the sedimentary rocks of the Cape Supergroup, which overlie the basement Malmesbury Group and Cape Granite Suite. Theron et al. (1992) noted that the landscape has developed mostly by erosion of the Malmesbury Group and the Cape Granite Suite, with more resistant quartzitic sandstone of the Table Mountain Group forming the mountains. The low-lying areas between mountains are generally fertile as they contain the weathered loamy soils. An overview of the geological events reflected in the rock record of the study area will be discussed.

### 2.2.2 General geology of the Cape Town area

The Cape Town metropolitan area is divided into multiple municipalities, this is from Cape Point in the southwest, Somerset West in the southeast, and Atlantis in the north, and includes to the south False Bay. All the geological units within the city of Cape Town area will be discussed, as the springs are located in this area, from the basement rocks to the youngest formations of the Cenozoic sedimentary deposits (Table 3).

Malmesbury Group

The main rock units exposed, north, and northeast of Cape Town belong to the Malmesbury Group (Geological-Survey, 1984). These rocks are exposed where the Cape Supergroup has been eroded away, typically over most of south-west cape. The Malmesbury Group is also exposed at the lower slopes Table Mountain area; the quality of the actual outcrops is very poor due to coverage by the Quaternary sediments and mountain scree. The Neoproterozoic age Malmesbury Group is the oldest unit in the area. The Malmesbury Group was deposited and intruded by the Cape Granite Suite; therefore, deposition, deformation, and metamorphism of Malmesbury Group occurred between 1.2 Ga and 510 Ma (Belcher & Kisters, 2003). They are generally composed of low-grade, metamorphosed volcanic-sedimentary formations, intruded by syn- to post-orogenic granitoid (Gresse, et al., 2006). They were placed during the construction of the supercontinent Gondwana.

The Malmesbury group which consists mostly of deformed metamorphosed volcanic-sedimentary formations occurs in three tectonic terranes, separated by two northwesterly striking major fault zones (Theron, et al., 1992). The southwestern Tygerberg Terrane and central Swartland Terrane are separated by the Saldanha-Stellenbosch fault, and the central Swartland terrane and northeastern Boland terrane by the Piketberg-Wellington fault zone (Gresse, et al., 2006). The rock formations of the Boland terrane are considered to be distal facies of rift successions, while the thick turbidite successions of the Swartland terrane and Tygerberg terrane reflect deeper water conditions and were deposited partly on oceanic crust in an evolving ocean/continental margin basin marked by increasing sea levels and reduction of continental freeboard (Rozendaal, et al., 1999). The Tygerberg terrane consists of the Tygerberg Formation and the Boland terrane is made up of the Porterville and Piketberg Formations. The Swartland terrane consists of five formations; Franschhoek Formation, Moorreesburg Formation, Bridgetown Formation, Klipplaat Formation and Berg River Formation.

**Table 3. Stratigraphy of the Cape Town area, produced based from simplified Cape Town explanation book sheet 3318 (1:250 000).**

| Age | Supergroup | Group | Formation |
|---|---|---|---|
| Quaternary (~1.8-present) | Cenozoic deposits (Mountain Scree) | | |
| Ordovician-Devonian (~490-~360 Ma) | Cape Supergroup | Table Mountain | Rietvlei |
| | | | Skurweberg |
| | | | Goudini |
| | | | Cedarberg |
| | | | Pakhuis |
| | | | Peninsula |
| | | | Graafwater |
| | | | Piekenierskloof |
| Namibian-Cambrian (~1000-~545 Ma) | Basement (Malmesbury Group & Cape granite Suite) | | |

The Granites

The Cape Granite Suite intruded during the formation of the Saldania Belt. These intrusions intruded into metasedimentary and metavolcanic rocks of Neoproterozoic age, the Malmesbury Group (Scheepers & Schoch, 2006). The Cape Granite Suite occurs as multiple intrusions of series of plutons and batholiths. Although composed mostly of granitic plutons, there is quite a range of rock types and intrusive forms in the Cape Granite Suite. A number of granite variations occur in each pluton. In the southwestern Cape, the Cape Granite Suite is subdivided into six major batholiths; Saldanha-Vredenburg, Darling, Malmesbury, Paarl-Wellington, Stellenbosch-Kuils River, and Peninsula (Harris, et al., 1997). Individual plutons have been classified as A-, I- and S-type granites on the basis of petrography, chemical composition, and oxygen isotope composition (Harris et al., 1997; Rozendaal et al., 1999; Scheepers & Schoch, 2006). Each granite type is found on a specific terrane of the Malmesbury Group. The S-type granitoids dominate in the western Tygerberg tectonic terrane, the I-type granitoids in the central Swartland terrane as well as the eastern Boland terrane, and the A-types are intrusive in both the Swartland and Tygerberg terranes (Scheepers, 1995).

The plutons of the Cape Granite Suite have been dated from very late Neoproterozoic to late Cambrian. The granites have also been divided into phases. The phase I, early syn-tectonic batholith reflects overall crustal sources, reflects S-type granites. The phase II, late to post-tectonic pluton, reflects I-type granites, while the late tectonic A-type Pluton indicates a shift from the evolution of dominantly metasedimentary to dominantly Mesoproterozoic sources and this was phase III (Silva, et al., 2000). The different phases are also associated with a certain type of granite, s-type granites in phase I, I-type granites in phase II, A-type granites and intermediate and mafic plutons in phase III, (Scheepers, 1995), summarised the phases age as following; phase1 S-type (600-540 Ma), phase 2 I-type (560-520 Ma) phase 3 A-type (520-500 Ma).

### The Cape Supergroup

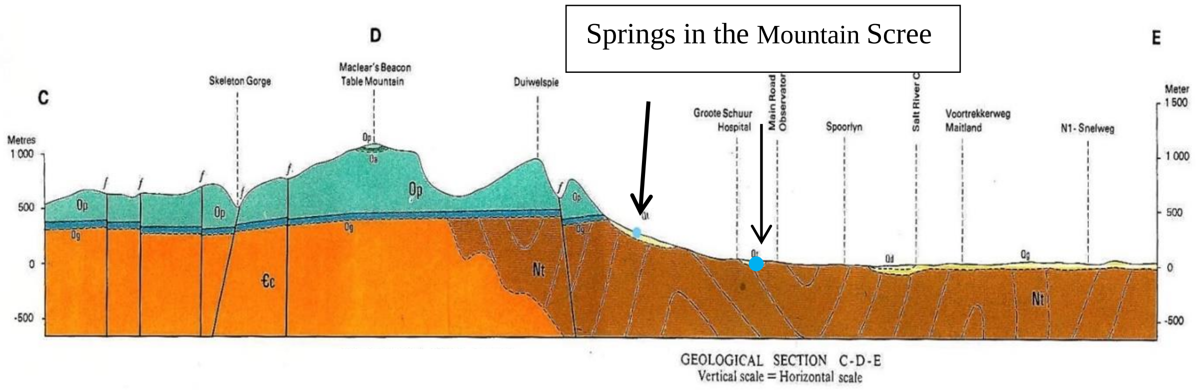
The Cape Supergroup dominates the geology of the Western Cape, extends into the Eastern Cape, and is represents three groups: the basal Table Mountain Group, Bokkeveld Group, and the Witteberg Group. The Table Mountain Group and the Bokkeveld Group are represented in the geology of Cape Town. Following the formation of the Saldania Belt, a suite of small rift basins was formed. Sedimentary rocks of the Cape Supergroup were deposited on a passive continental rift basin in a variety of terrestrial and shallow marine shelf depositional environments, from the early Ordovician until the mid-Carboniferous (Shone & Booth, 2005). The Supergroup represents approximately 170 Ma years of earth history, from the Early Ordovician (~500 Ma) to the mid-Carboniferous (~330 Ma) (Thamm & Johnson, 2006). The Cape basin formed within the continental interior of Gondwana supercontinent  Tankard et al. (2009) wrote that subsidence resulted from the vertical motion of rigid basement blocks and crust faults, and added that basin records show a three-stage evolution consisting of crustal uplift, fault-controlled subsidence, and long periods of regional subsidence largely unaccompanied by faulting or erosional truncation. Cloetingh & Lankreijer (1992) noted two episodes of accelerated subsidence, starting at about 465 and 390 Ma respectively, which are recorded in the Cape Supergroup. The Cape Supergroup strata have palaeontological significant due to the diverse trace fossil assemblages in the lower Table Mountain Group (Thamm & Johnson, 2006). The fossils were used for dating some of the rock formations.

### The Cenozoic sedimentary deposits

The Cape Flats and the coastline between Cape Town and Saldanha are covered by the sediments of Quaternary age overlying disconnected Neogene deposits of which little is known except for boreholes and quarries. These deposits are called the Sandveld Group. Neogene Deposits are buried by the present sea level. During Tertiary transgression and regression of sea level, thin deposits formed, some of which were preserved on land in deeper erosional basins, the Neogene gravel, sand and clay beds of the Elandsfontyn Formation, Saldanha Formation (Prospect Hill Formation) and Varswater Formation (Theron, et al., 1992).

### Mountain Scree

Scree deposits can be several meters or more in thickness in some places, consisting of and terrace gravel and coarse-grained sands overlie the mountain lower slope of the Table Mountain. The deposits generally consist of angular blocks of Table Mountain Group from several centimeters to a few meters in diameter, with varied sand and gravel. Large granite boulders sometimes also occur in scree fans of the Cape Peninsula. The scree gradually grades downhill into gravel/sand of similar composition with a decrease in the number of size of the boulders (Theron, et al., 1992). The mountain scree consists mostly of quartzite fragments. These deposits can occur as a result of the process associated with the weather changes causing erosion of quartzite and other formations. Gravity also drives the transportation (downward movement) of fragments along the steep slope which results in the formation of mountain scree. Lastly, chemical weathering of coarse fragments contribute to the mountain scree. The investigated springs are found in the scree on the lower slopes of Table Mountain and are situated in the deeply weathered metasedimentary strata of the Neoproterozoic Tygerberg Formation of the Malmesbury Group (Figure 6). Theron et al. (1992) wrote the scree deposits were possibly laid down by an Early Pleistocence.



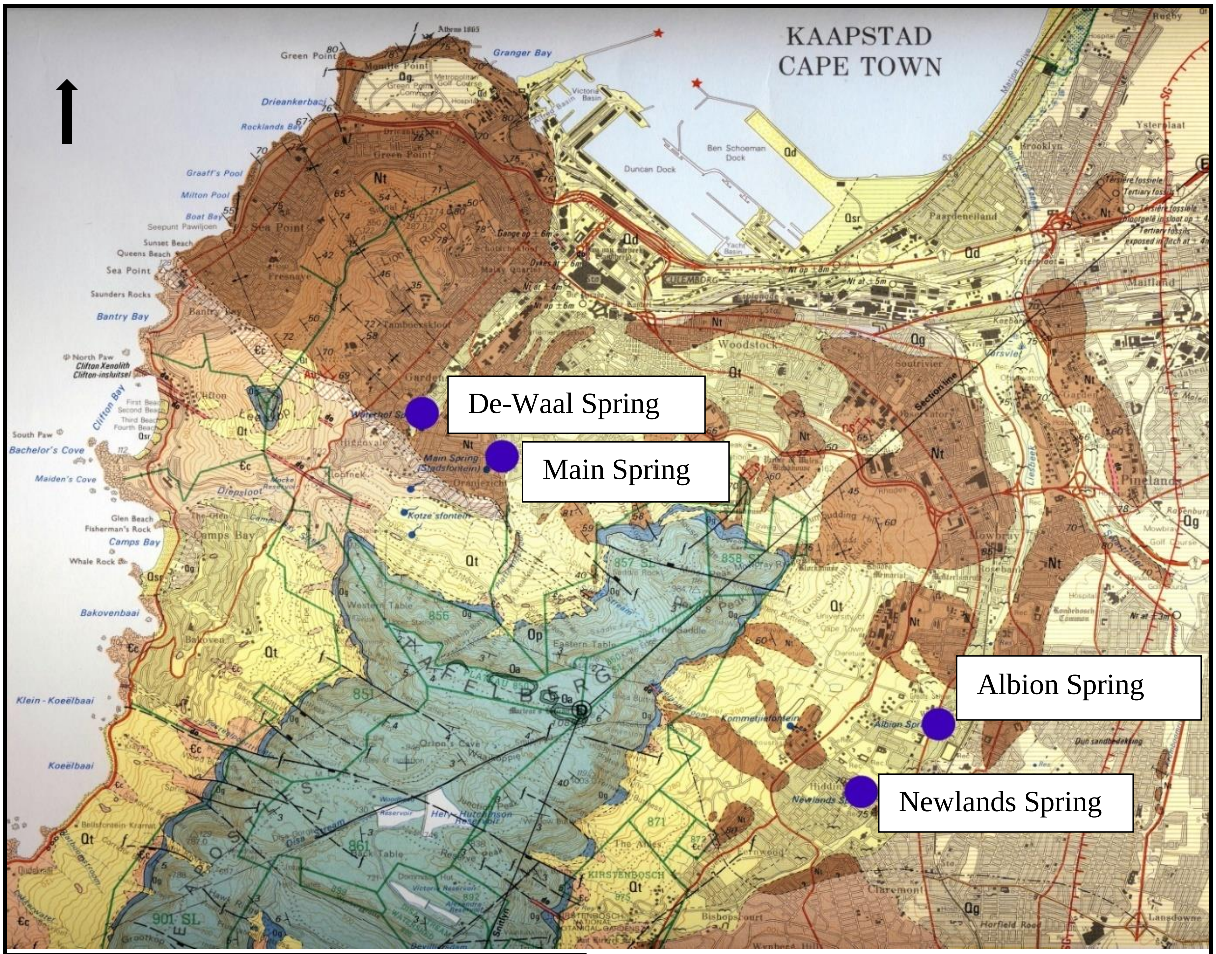
| Legend | | |
|---|---|---|
| **Group** | **Formation** | **Key** |
| Sandvlei | | Qt |
| Table Mountain | Pakhuis | Oa |
| | Peninsula | Op |
| | Graafwater | Og |
| | Cape Granite Suite | єc |
| Malmesbury | Tygerberg | Nt |

**Figure 6. Cross-section of the geology of the study area (cross-section from 3318 CD Cape Town map).**

### 2.2.3 Lithostratigraphy in the study area

Malmesbury Group

Malmesbury Group outcrops are exposed on the lower slopes of Table Mountain. The exposure is more prominent towards the coastline, from Ganger Bay to Sea Point. The rock types found in the group are mainly greywacke, siltstone, limestones, and chert. The formations within the group are characterised by rhythmic alternations of greyish to greenish medium to fine-grained greywacke, phyllitic shale and siltstone, immature quartzite and conglomerate beds (Gresse et al., 2006; Belcher & Kisters, 2003; Hardnady et al., 1985).The Tygerberg Formation is confined in the southwestern section of Cape Town; this forms part of where the springs are located.



| Group | Formation | Key |
|---|---|---|
| Sandvlei | Alluvium/Scree | Qt/Qd |
| Table Mountain | Pakhuis | Oa |
| | Peninsula | Op |
| | Graafwater | Og |
| Cape Granite Suite | Cape Peninsula Granite | єc |
| Malmesbury | Tygerberg | Nt |

**Figure 7. Geological map of the study area, showing the outcrop of the Malmesbury Group, Table Mountain Group and cenozoic sediments deposits (map from 3318 CD Cape Town geology map).**

Cape Granite Suite

The coarse-grained igneous rock of the Cape Granite Suite underlies the major part of the Table Mountain area. The outcrops are mostly exposed along the coastline from Sea Point southwards to Llandudno. The granite intruded the Malmesbury Group. The Granite-Malmesbury contact is exposed in Sea Point and the contact between Granite and the Table Mountain Group is located several meters above Kloofnek. Theron et al. (1992) identified three varieties of granite around the Cape Peninsula, firstly the grey coarse-grained, porphyritic biotite granite, characterised by large twinned orthoclase phenocrysts, forms the major part of the Cape Peninsula pluton and then the fine-grained, non-porphyritic granite which is a very uniform light-grey muscovite granite, which contains some biotite.

Table Mountain Group

The lithostratigraphy of the Table Mountain Group in the study area is represented by three formations of the Group, not all units are represented in this area (Figure 7). The basal formation Piekenierskloof Formation does not occur, the oldest formation of the Table Mountain Group to occur in the area is the Graafwater Formation. The Graafwater Formation rest unconformity on the Cape Granite and the Malmesbury Group and is overlain by the Peninsula Formation. The Pakhuis Formation overlies the Peninsula Formation, on top of Table Mountain near the Maclear's Beacon, is the exposed outcrop of the Pakhuis Formation. Graafwater Formation is characterised by purple to reddish brown, thin-bedded, ripple-marked sandstone, siltstone and shale make-up this formation, which is best exposed on the Cape Peninsula. Depositional structures are abundant in the Graafwater, including lenticular and flaser bedding, a wide variety of water ripple marks, stream lineations, desiccation cracks, ball-and-pillow structures, and clay pellet conglomerate lenses (Rust, 1967; Theron et al., 1992). The Graafwater Formation sediments are generally considered to have originated in a shallow marine tidal flat setting characterised by intermittent exposure (Shone & Booth, 2005).

The Peninsula Formation is the dominant formation of the Table Mountain Group, there is massive beds of Peninsula Formation preserved in the field. The sandstone is light grey, medium to coarse grained, mainly planar bedded, but commonly with trough cross bedding, usually thickly bedded, but in places massive or thinly bedded (Shone & Booth, 2005). These strata consist of well-bedded, high cliffs towards the top of Table Mountain. It is generally thick bedded, but massive and thinly bedded units also occur. The rock consists primarily of quartz grains, a small percentage of feldspar, occasional chert grains, and sericite and clay minerals as a matrix (Theron, et al., 1992). The Pakhuis Formation occurs only in the western half of the Cape Basin, west of Swartberg Pass (Thamm & Johnson, 2006). The Pakhuis Formation is preserved on top of Table Mountain. The Sneeukop Member is massive bedded diamictite and rests on essentially horizontally bedded units of the Peninsula Formation which often contain thin beds of the conglomerate with well-rounded vein-quartz pebbles right at the top. The Sneeukop Member usually weathers into yellow-brown colour. The uppermost thick-bedded sandstones, on which the beacon rests, represent the local equivalent of the Oskop Member (Theron, et al., 1992). Ice movement, as inferred from tillite fabrics and soft sediment deformation features, appears to have been variable, but with a strong southerly component, the Pakhuis Formation is certainly glacial in origin (Shone & Booth, 2005).

### 2.2.4 Geology- Structure

The tectonic history starts from the formation of Saldania Belt during the formation of the supercontinent Gondwana. Followed by the deformation of strata of Neoproterozoic age (Saldania Belt) accompanied by intrusions of granitic plutons (Cape Granite Suite) between ~560 and ~510 Ma, overlapping the Cambrian-Proterozoic boundary (Hunter, et al., 2006). The Cape Fold Belt (CFB), of which covers most of the Western Cape Province was formed. The CFB is a set of nearly parallel ranges of sandstone folded mountain of Cambrian-Ordovician age.

Structure around Table Mountain

The sand, silt, and mud deposits of the Table Mountain Group were folded during the formation of the Cape Fold Belt, and faults cut across the rock layers (Theron et al., 1992; Shone & Booth, 2005). The Cape Peninsula area is made up of synclines and anticlines. Synclines are folds of rock units in which the units slope upwards from the axis and the younger units are closer to the center of the structure, for example the Table Mountain area is a syncline fold with younger Table Mountain Group at the center, and the anticline fold has been eroded away forming the Cape flats with the older basement Malmesbury group at the center. The greater Cape Town present landscape is due to erosion of soft rocks such as the silt and mud deposits of Table Mountain Group, forming low lying areas like the Cape Flats surrounded by high residual hard sandstone deposits. The contact-metamorphic effect of Cape granite intrusion in the Tygerberg Formation is best known along the beach from Granger Bay to Sea Point (Geological Survey, 1984).

## 2.3 Climate and weather

### 2.3.1 Climate

The study area experiences a typical Mediterranean climate with moderate temperatures and winter rainfall. The summers are warm and dry, while the winters are cool and wet. The area falls in the highest rainfall zones in South Africa (SAWS, 2017). The rainfall usually follows a high altitude distribution. There is more rainfall in mountainous areas, as the results many low-lying urban areas are unable to make use of the available high rainfall. The dominant wind direction is the North West and South East. The prevailing wind in summer is known as the South-easterly (south-east) and during the winter the northwest wind precedes the cold fronts that bring rain to the local area (Atkins, 1970). The climate and weather of an area are important factors in the hydrogeology of an area.

### 2.3.2 Weather

Rainfall

The annual rainfall received in Cape Town differs from season to season. The summer months receive less rainfall than the winter months. There is also a difference in the amount of rainfall received at UCT, which is situated on the slope of Table Mountain and the rainfall recorded at the Cape Town International Airport, which is located at Cape Flats. (Figure 8) shows that at some months UCT seem to get triple the amount of rainfall received at the Cape Town International Airport, for example for the month of July from 2012-2016 UCT has received more than double the rainfall amount received at the airport: 2012 - 293/92 mm, 2013 - 184.5/43.6 mm, 2014 - 243.2/109.4 mm, 2015 - 187.4/87.8 mm, 2016 - 234.3/83 mm respectively. During the rainy season (April to September), UCT received on a monthly average almost three times more rainfall than the recorded at the Cape Town International Airport.

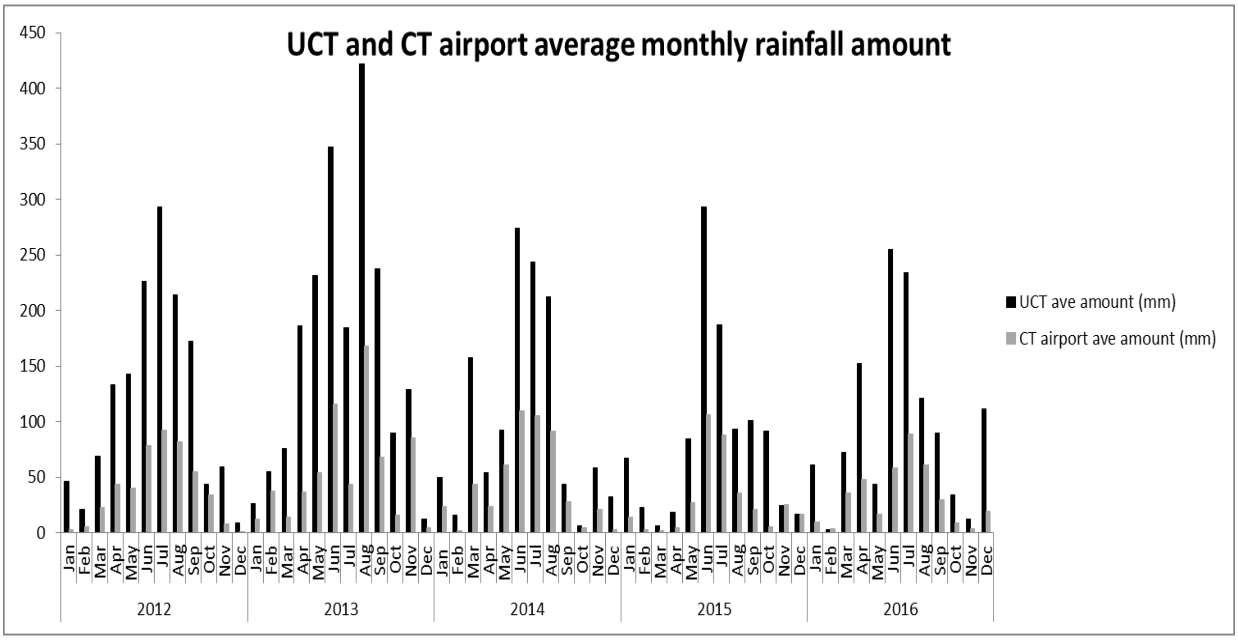


**Figure 8**. **Diagram showing the average monthly rainfall from 2012-2016 for UCT and Cape Town International Airport, data from SAWS (2017) and Department of Geological Sciences (UCT).**

The southwestern Cape coast receives most of the annual rainfall in winter, moving away from southwestern Cape further north, the winter rainfall decreases until desert conditions. The rain results from the Westerly wave, but the summer rainfall is not associated with the Westerly Wave. Westerly Wave carries frontal depressions (low-pressure systems) from the middle latitudes, at around ~60ºS in the South Atlantic Ocean, and move north-eastwards until they begin to move south-eastwards. The low-pressure systems usually pass the southern tip of Africa during summer (Kelbe, 1988). During winter the westerly wave shirt towards the north and the low depression systems (cold fronts) reaches the interior of the country (Figure 10). Westerly wave features a warm front and cold front, where air masses of different temperature meet, and the whole system rotates clockwise in the southern hemisphere (Rossouw, 1989).

Temperature

The average temperature for Cape Town generally ranges from 25º C to 32º C in summer and 10º C to 18º C in winter. (World Weather Online, 2017). February is the hottest month and the coldest is June. Due to the location of the city, along the coastline temperature is more consistent. The ocean and humid air keep the temperature relatively moderate throughout the year. (Figure 9) is a temperature-rainfall graph; the graph depicts a negative correlation between the temperature and rainfall. Cape Town receives the highest rainfall during the months with low temperatures.

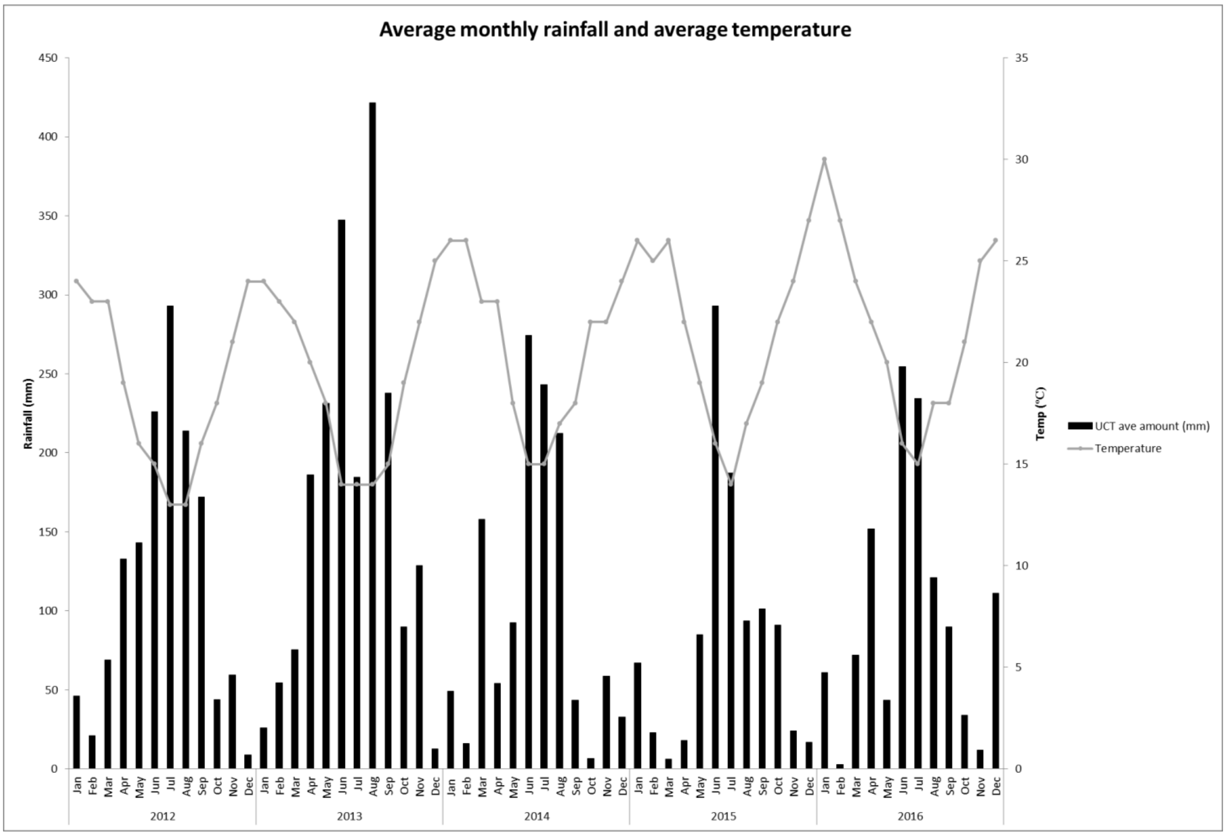
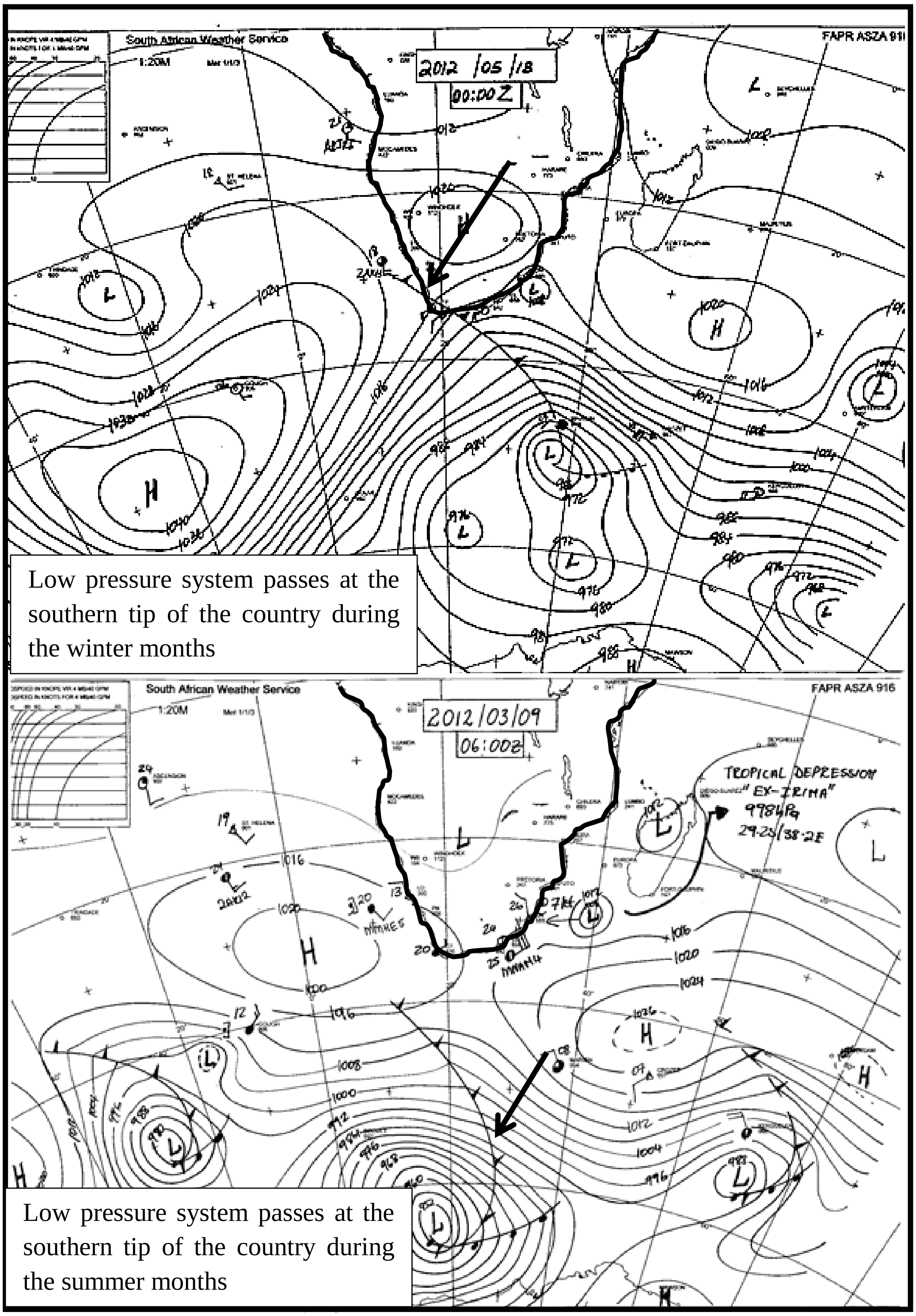


**Figure 9. Plot of the average monthly rainfall, data from Department of Geological Sciences (UCT) and average monthly temperatures, data from world weather online (2017).**



Low pressure system passes at the southern tip of the country during the winter months

Low pressure system passes at the southern tip of the country during the summer months

**Figure 10. Example of synoptic charts for the winter and summer months, showing the position of the low pressure system, charts from SAWS.**

## 2.4 Hydrogeology

### 2.4.1 Regional hydrogeology

Groundwater occurs in two types of aquifer systems in the study area, fractured and intergranular aquifers. In the fractured aquifers, the rock units have widespread fracturing and joining, groundwater is stored in the fractures, joints, bedding planes. The aquifers in the study area include the fractured quartzitic Peninsula Formation Aquifer of the Table Mountain Group Aquifers, the Cape Flats Aquifer, and the mountain scree Aquifer. The Cape Flats Aquifer (intergranular aquifer) is a primary aquifer, while the Peninsula Formation Aquifer and the mountain Scree Aquifer (fractured aquifer) are secondary aquifers. An aquifer can be a part of one rock formation (hydrostratigraphy units) or several rock formations. The lithological units can be aquifers and aquitards. The aquifer is the fundamental unit, contains groundwater and the aquitard acts as a barrier. Aquitards having sufficient thickness to retard the flow across them in considered another important criterion for such a classification (Al-Aswad & Al-Bassam, 1997). In the study area, the basement Malmesbury Group is an aquitard. The groundwater in the Malmesbury Group tends to be of poor quality and have poor yields from boreholes.

### 2.4.2 Local hydrogeology (Hydrostratigraphy)

Table Mountain aquifer

The Table Mountain Group aquifers systems have the potential for bulk water supply in the Western Cape provinces. The Table Mountain Group is not a simple, single aquifer with a neat geometrical shape, but rather a system of multiple aquifers, from different hydrostratigraphy units. Table Mountain Group Aquifer system in the Table Mountain area consists of the Peninsula Formation Aquifer (Table 4). The Peninsula Formation consists of pure quartz arenites with a very low primary porosity due to the cementation of individual sand grains. Due to brittle fracturing deformation, as well as higher fracture frequencies and a well-developed secondary porosity which serves as the main groundwater storage space and flow path has developed (Jia, 2007). The upper most part of the Table Mountain, the Peninsula Formation is overlain by the glaciogenic Pakhuis Formation, which is a few meters in thickness (Thamm & Johnson, 2006), all these formations acts as aquitards. Direct recharge, through infiltration, recharges the Peninsula Formation Aquifer. The Peninsula Formation Aquifer discharges mainly into the ocean along the major fault systems in the Peninsula Formation, at high-lying springs, or seeps zones.

**Table 4. Hydrostratigraphy of the Table Mountain Aquifer in the Table Mountain area.**

| Group | Formation | Aquifer |
|---|---|---|
| Bokkeveld Group | | Aquitard |
| Table Mountain | Pakhuis | |
| | Peninsula | Aquifer |
| | Graafwater | |
| | Piekenierskloof | |
| Basement (Malmesbury Group & Cape Granite Suite) | | Aquitard |

Mountain Scree Aquifer

Groundwater commonly discharges into surface water bodies or the sea. However, discharge can take place at points, such as springs and deep zones. Precipitation that does not infiltrate into the TMG groundwater system accumulates in the mountain scree, and this is what recharges the mountain scree aquifer. Scree deposits on the slope consist of sand, gravel and other unconsolidated materials. Lateral recharge can occur, where groundwater from one aquifer discharge into the overlying aquifer (Umvoto Africa, 2012). This could possibly be what is taking place at the slope of the Table Mountain. Shallow circulating springs that occur in the mountain scree (Figure 11) might be sourced entirely from the mountain scree Aquifer or the springs might be maintained in part by overflow from the Peninsula Aquifer. Diamond (2015) wrote the rainfall infiltrates the Peninsula Formation and recharges the Peninsula Aquifer; at the same time the rainfall also falls on the Scree on the lower slope and recharges the Scree Aquifer. Some of the water from the Peninsula Aquifer after some time, recharge the Scree Aquifer as the water slowly flow from the high altitude Peninsula Aquifer into the shallow laying Scree Aquifer at the lower slope.

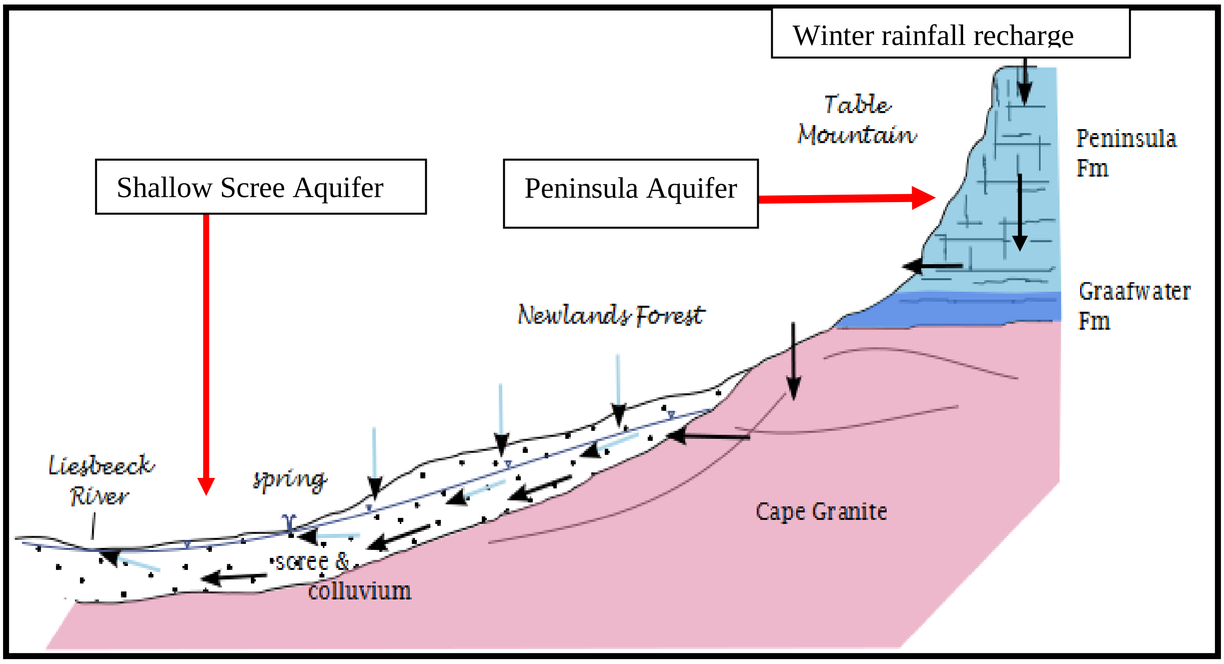


**Figure 11. Sketch cross section of the springs in the mountain scree, altered diagram from Diamond (2015).**

# Chapter 3 Materials and methods

This chapter describes the methods used for collection of samples; samples preparation, laboratory analysis and the data accuracy/correlation see the methodology flowchart (Figure 12). The locations of all the sample sites have been shown in (Table 2) and (Figure 4).

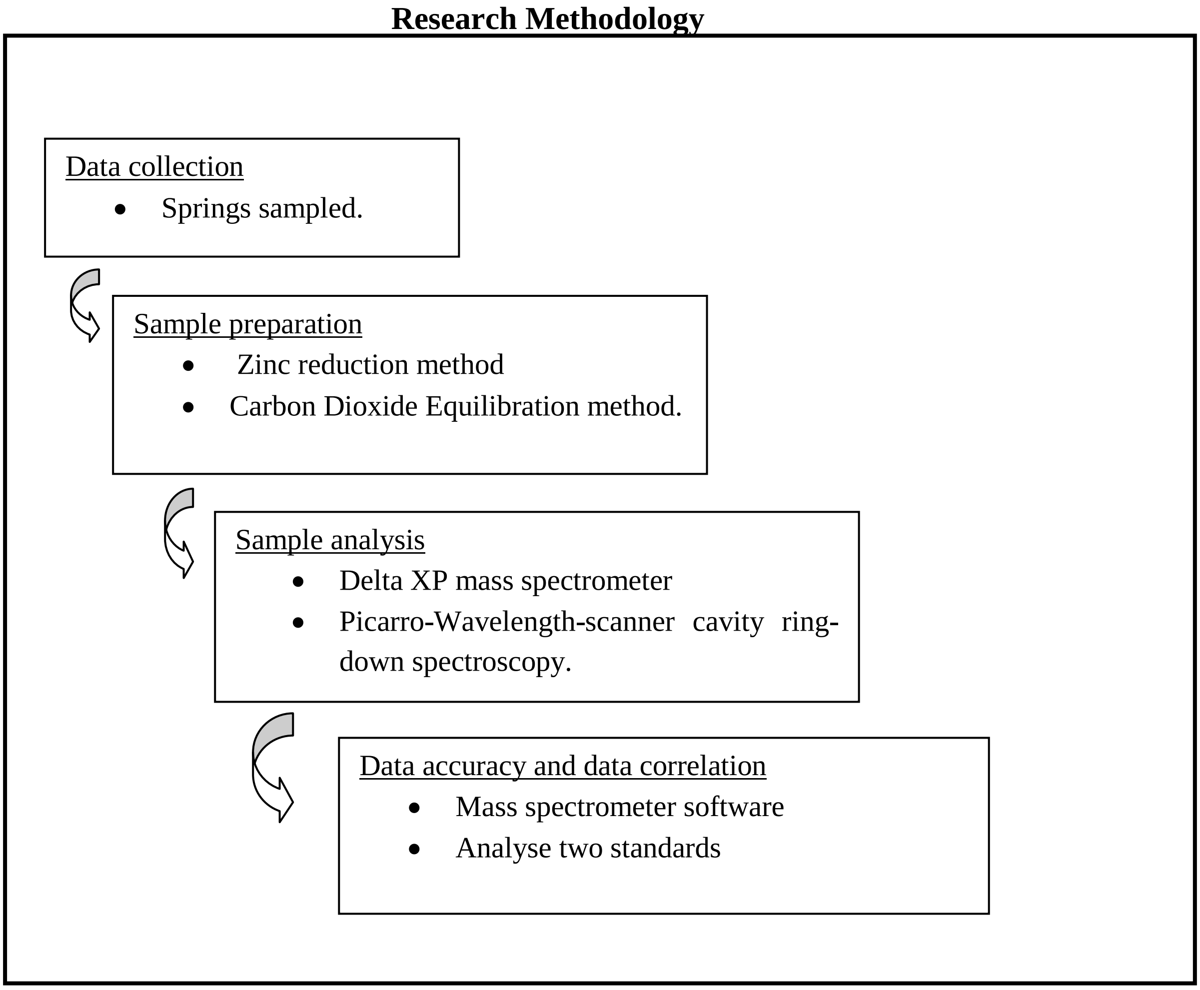


**Figure 12. Research methodology depict in a flowchart.**

## 3.1 Fieldwork

### 3.1.1 Sample collection

Rainfall

The rainfall was collected at the University of Cape Town. The data used for this thesis was collected from 1995 to 2016. Data from 1995 to 2008 was reported in (Harris, et al., 2010). The rain gauge is stationed on the rooftop of the Department of Geological Sciences at UCT. The gauge is easily accessible, rainfall is collected daily (if it rained) and emptied into a glass jar, from which a sample is taken for analysis. The monthly rainfall amounts were recorded. The rain gauge used for the sample collection was a standard plastic rain gauge.

### Springs - Groundwater

Groundwater was sampled from four springs (Figure 13), The De Waal spring, Newlands spring, Albion spring, and the Main spring. (Figure 13) (a) is the Albion spring, (b) Newlands spring, (c) De Waal spring, the spring flows into the De Waal reservoir and (d), (e) and (f) the Main spring, which is water from several springs in the field of springs, mixed together. The altitudes of which each spring is situated are recorded in (Table 2). Harris et al. (1999) reported an estimation of yields for Main spring, Albion spring and Newlands spring, all the three springs yield is >1000 l/min. Wu (2008) reported the following yields for 2008; Albion spring $3.0 \times 10^6$ l/day, Newlands spring $1.55 \times 10^6$ l/day, Main spring $2.2 \times 10^6$ l/day, there was no data for the De Waal spring, but from the litre per minute estimations made by Harris et al. (1999), the De Waal spring is estimated to have a yield of $1.4 \times 10^6$ l/day. Springs were sampled at or as near as possible to the source, in the cases where the spring was piped (PVC pipe) from the source (Figure 14).Various items of field equipment were used to obtain the water sample from the source, (Figure 15) depicts all the field equipment used. A bucket was used to collect the water from the spring and a water bailer would be used if the spring water level was low or could not easily be reached. The water is clean; there was no need to filter the springs' water, especially for stable isotope measurements. Unfiltered water samples were collected and immediately sealed and stored in glass or plastic bottles ranging from 10-100 ml capacity, they were filled up to the brim to avoid fractionation through evaporation and then sealed with a plastic cap (Figure 16). After collection, spring samples were stored at room temperature before they were prepared for the measurement of oxygen and hydrogen isotope ratios.


9a) Albion spring outlet 9b) Newlands spring outlet


9c) De Waal spring 9d) De Waal Reservoir


9e) Field of springs 9f) Main spring (where all springs mix)

**Figure 13. Photos of the four springs sampled; (9a) the Albion outlet, (9b) Newlands spring outlet, (9c) De Waal spring outlet, (9d) De Waal reservoir, (9e) field of springs at the Main spring and (9f) the Main spring (where all the springs mix).**

**Figure 14. Newlands spring water piped from the source, using a PVC pipe.**
**Figure 15. Field equipment used during sampling.**

### 3.1.2 Electrical conductivity (EC) and temperature (T) measurement

At the spring sites, an EC and temperature meter were used to measure electrical conductivity (EC) and the temperature (T). From a sample collected in the bucket, a portable WTW- conductivity multimeter with a TeltraCon350i probe was used to measure the EC and temperature (Figure 17). The EC and temperature values were recorded on a field sheet paper on site. The EC is one of the parameters that can be used to determine the quality of the water. In a laboratory at the Department of Geoscience Sciences, the EC meter was used to measure the EC of tap water, tap water EC was measure from ten water samples and the results were always almost the same, with an average of 164.44 µS/cm. The EC values are reproducible because the EC meter measuring EC from the 10 tap water samples obtained very similar results. The same test was used on tap water mixed with table salt, 10 teaspoon of salt was mixed with 1 liter of tap water, and the average mean values was of 32.61x$10^3$ µS/cm (Table 5). The EC meter was not calibrated in the field but standard solutions made up in the lab from KCl following the ECN technical note 3 protocol utilising standards with EC of 1411 and 76 µS/cm suggest that any corrections is minimal (~1 µS/cm at 250 µS/cm).

**Figure 16. Collecting water sample into a water bottle.**
**Figure 17. Using the EC and temperature meter to measure EC and temperature.**

**Table 5. Test of precision of EC measurements. One is tap water of approximately the EC of the springs, the other is salt water solution. Measurements made in an identical way to data collected in the field.**

| Samples | Tap Water (µS/cm) | Salt Water (µS/cm) |
|---|---|---|
| | 161.2 | 34.1x$10^3$ |
| | 161.7 | 33.2x$10^3$ |
| | 162.3 | 32.6x$10^3$ |
| | 165.8 | 32.5x$10^3$ |
| | 166.5 | 32.4x$10^3$ |
| | 164.8 | 32.7x$10^3$ |
| | 165.4 | 32.3x$10^3$ |
| | 165.4 | 32.4x$10^3$ |
| | 165.6 | 32.2x$10^3$ |
| | 165.7 | 31.7x$10^3$ |
| Average | **164.44** | **32.61x$10^3$** |
| STDEV | **1.932** | **0.614x$10^3$** |

## 3.2 Stable isotope analysis

### 3.2.1 Sample preparation

Water samples are stored at room temperature before they are prepared for measurement of oxygen and hydrogen isotopes ratios. Water samples are prepared for the analysis of oxygen and hydrogen in the Department of Geological Sciences at UCT (extraction lines used for both the oxygen and hydrogen are located at the department), and the mass spectrometer measurements are performed at the Archaeology Department, but this has change as from November 2016 Picarro-Wavelength-scanned cavity ring-down spectroscopy was used for the measurements of oxygen and hydrogen isotopes ratios. For the determination of the oxygen and hydrogen isotopes, water samples need to be reduced into a gas so they can be used in the mass spectrometry. For hydrogen, the zinc reduction method used was based on the method of Coleman et al. (1982). For oxygen, the $CO_2$ equilibration method by Socki et al. (1992) is used.

Hydrogen Isotopes - Zinc Reduction Method

Samples are prepared for deuterium analysis using the Zinc Reduction Method. A break-seal tube is loaded with 100±3 mg of zinc (zinc shavings). The tube is then placed onto the vacuum line and evacuated see (Figure 18). The tube is heated with hot air gun, the zinc begins to vaporise and re-deposits higher up on the tube. The tube is then removed from the line and allowed to cool down then a 2µl of sample water is collected into a 2µl capillary tube. The microcapillary tube containing the sample water is then dropped into the tube. The tube is then placed back on the line and evacuated, immediately after the lower portion of the tube is immediately immersed in liquid $N_2$ for 2 minutes. Once the sample water is frozen, the evacuation of the line is opened, and the non-condensable gases are pumped out. The tube is then sealed with an oxygen-propane blow torch. Prior to the mass spectrometer analysis, the tube is placed in a furnace at 450° C for 30 minutes, in order to completely reduce the sealed water with the zinc reagent, to produce ZnO and $H_2$ from $H_2O$ Coleman et al. (1982).This tube could then be loaded into the mass spectrometer for the analysis of the hydrogen gas.

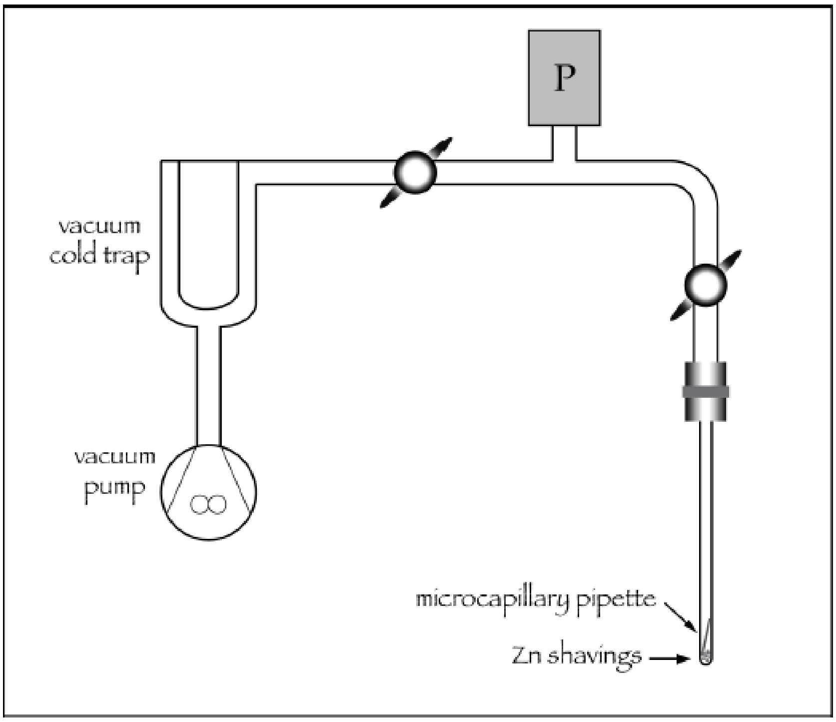


**Figure 18. Vacuum line for preparing water samples for hydrogen isotope analysis, diagram from Diamond (2015).**

Oxygen Isotopes - Carbon Dioxide Equilibration Method

The method used is based on the original methodology developed by Epstein and Mayeda (1953) and also described in Socki et al. (1992). Sample preparation for oxygen isotope analysis was done by the method of equilibrating sample was with $CO_2$. A disposable, 7 ml vacutainer test-tube is placed onto a vacuum line via a hypodermic needle and then evacuated see **(**Figure 19). About 0.3 atm of $CO_2$ is loaded into the vacutainer from a tank of medical grade $CO_2$. The vacutainer is removed from the line and injected with ±2 ml of sample water. To allow for isotope equilibration between $H_2O$ and $CO_2$, the vacutainer is fixed to an automated shaker submerged in a 25°C bath and is shaken for two hours. It is then left to equilibrate overnight. The vacutainer is then placed onto the line with a hypodermic needle just piercing the rubber seal and not penetrating the vacutainer itself, and air in the needle pumped out. The sample water in the vacutainer is then submerged in liquid $N_2$ for a period of five minutes to ensure complete freezing of the $H_2O$ and $CO_2$. The needle is then fully inserted into the vacutainer, and the line is evacuated, a non-condensable gas is then evacuated out of the system. The sample water within the vacutainer remains frozen with liquid $N_2$ during the evacuation stage. The liquid $N_2$ which acts as a trap around the vacutainer is removed and replaced with frozen isopropanol. This action vaporises the $CO_2$, which expands into the line and is re-frozen towards a metal finger using another trap of liquid $N_2$. Unwanted gases can again be pumped away and the vacutainer is closed from the line. The liquid $N_2$ is removed from the cold finger and is immediately replaced with the frozen isopropanol. The $CO_2$ is allowed to warm up and expands into the line, and refrozen with liquid $N_2$ into the second cold finger attached to a pressure transducer.

This second cold finger is then shut off from the line, and once the liquid $N_2$ is removed, it is heated to room temperature in order to measure the voltage which can be used to calculate the number of micromoles of $CO_2$, and hence the yield. The yield is required to estimate whether or not there had been any leakage of $CO_2$ from the vacutainer. Assuming approximately the same amount of $CO_2$ had been let into the vacutainer the yields should be similar. The second cold finger is then re-opened to the line and liquid $N_2$ is placed around a break-seal tube in order to freeze in the $CO_2$. The tube containing the frozen $CO_2$ is then sealed under the vacuum with an oxygen-propane blow torch.

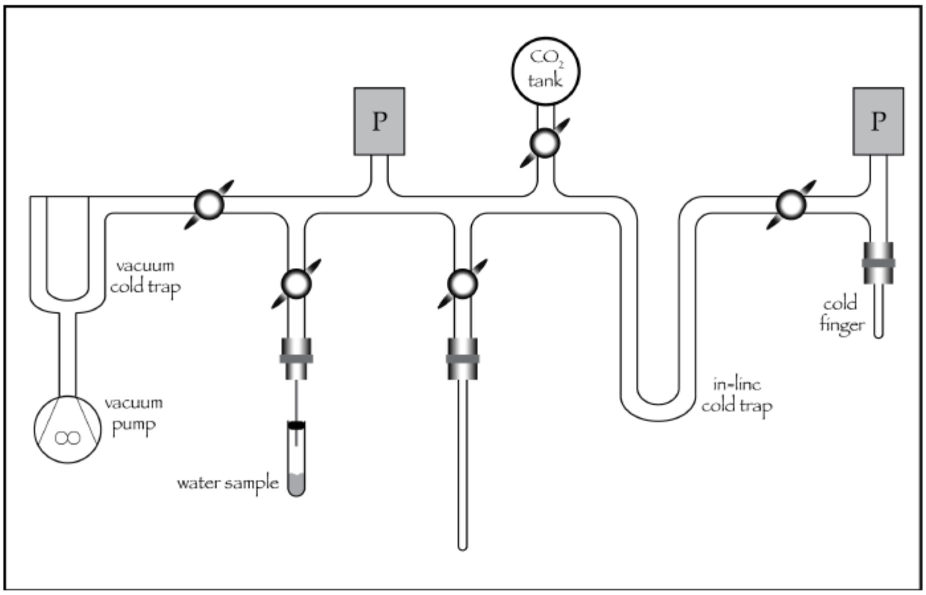


**Figure 19. Vacuum line for the preparing water samples for oxygen isotope analysis, diagram from Diamond (2015).**

### 3.2.2 Mass Spectrometry - Water isotope analyses

Sampled prepared were submitted for isotope analysis in the Delta XP Mass spectrometer located in the Archaeology Department. The mass spectrometer was used for conventional dual inlet analysis of hydrogen and oxygen isotope ratios at separate times. Isotope ratios of $CO_2$ and $H_2$ were measured Delta XP mass spectrometer, and the fractionation factor between $CO_2$ and water at 25ºC was assumed to be 1.0412 (Coplen, 1993). The data produced was recorded in the δ notation (Rsample/ Rstandard – 1)*1000 and R=D/H or $^{18}O/^{16}O$ and measured in per mil (‰).

<u>Standards</u>

For all isotope analyses, the internal isotope reference water standard was CTMP2010, which stands for Cape Town Millipore Water and Rocky Mountain Water (RMW) which is from water with a source in the Rocky Mountains near Salt Lake City (Table 6). CTMP2010 was calibrated at the Department of Geological Sciences using IAEA (International Atomic Energy Agency) standards SMOW and SLAP (Standard Light Antarctic Precipitation) and independently analysed. Two standards were used to correct for scale compression.

Standards used for oxygen and hydrogen isotopes

Ocean Water is used as the standard for all hydrogen isotope analyses and for most oxygen isotope analyses.

- Standard Mean Ocean Water (SMOW) as a standard. V-SMOW is an equivalent standard developed by a group in Vienna. The original SMOW supply may be completely used up.
- PDB (now VPDB) is a carbonate material used for oxygen isotopes in carbonate rocks.

**Table 6. Standards used in the study and their delta values, data from Harris et al. (2010) and Diamond (2015).**

| Standard | δD (SMOW) ‰ | $\delta^{18}O$ (SMOW) ‰ |
|---|---|---|
| CTMP2010 (Cape Town Millipore Water) | -7.4 | -2.74 |
| RMW (Rocky Mountain Water) | -131.4 | -17.38 |

### 3.2.3 Picarro–Wavelength-scanned cavity ring-down spectroscopy

Within three days after the samples were prepared for analysis, the samples were analysed by using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS). Analyses were performed on a water isotope analyser (L1102-i) from PicarroInc (Sunnyvale, USA). West et al. (2010); West et al. (2011) describes the steps of the procedure as follows; microliter quantities of sample water is injected into a vaporisation chamber and then passed into an infrared absorbance cavity. The isotope ratios (δD and $\delta^{18}O$) were calculated from the ring-down time at specific wavelengths using WS-CRDS.

The Picarro-Wavelength-scanned cavity ring-down spectroscopy differs from the Mass spectrometry. In conventional infrared spectrometers, trace gases provide far too little absorption to measure, limiting sensitivity to the parts per million at best. Cavity Ring-Down Spectroscopy avoids this sensitivity limitation by using an effective pathlength of many kilometres, it enables gases to be monitored in seconds or less at the parts per billion level, and some gases at the parts per trillion level (Picarro Surveyor, 2018).

### 3.2.4 Accuracy of the data and data correlation

Data from the mass spectrometer were corrected using the following method. The $H_3$ produced during the operation of the Delta XP mass spectrometer, which interferes with the measurement of the hydrogen isotope, had to be corrected. This was corrected by using software provided with the Delta XP mass spectrometer. The mass spectrometer measures the ratio of H-D to $H_2$ (mass 2/3). During ionisation in the source, some $H_3$ is produced, but the amount is directly proportional to pressure. Thus the mass spectrometer automatically measures mass 3/2 at different pressures and calculated the $H_3$ correction factor for the pressure at which the sample is run. Additionally, analysing two standards of differing δD and adjusting the difference to the correct one, also corrects for any $H_3$ formed. The other correction was for the fractionation of oxygen between $H_2O_l$ and $CO_2$, which at 25ºC has a fractionation factor of 1.0412 (Coplen, 1993).The correction was applied for the difference between the reference gas and the SMOW, CTMP (laboratory water standard) was ran with each batch of samples and used to correct for drift in the reference gases (Harris, et al., 2010). Standardisation similar to mass spectrometer method, two standards were used to correct for scale compression.

# Chapter 4 Results

## 4.1 Introduction

This chapter reports the results of data from the four spring samples from 2013-2016. The chapter will also report on 21 years record of hydrogen and oxygen isotope data of rainfall and the data are presented over time as monthly amounts. The datasets will be used to calculate line of the best fit local meteoric water line. Analysis of stable isotope data consists of finding correlations and this correlation defines the trend of the local meteoric water line (LMWL). The oxygen and hydrogen isotope data of the various water samples will be presented in forms of graphs and tables. Isotope data of the rainfall is presented and compared with the isotopic compositions of the four springs, the variations with time will also be reported. Springs isotope data is used to produce the best-fit lines and compared to the rainfall isotope data and local meteoric water line. The long-term variation in isotope composition of rainfall is used to estimate the recharge rate. The isotope data for the springs and the sampled rainfall is represented in (Table 7) to (

Table **13**).

## 4.2 Rainfall

For the purpose of this study data from 1995/6 to 2016/12 will be used to calculate the LMWL. To study or analysis, the hydrological impact of hydrogen and oxygen isotope ratios for long-term, the amount of rain for each month over the years must be known. All the rainfall samples data are in (Table 7). The apparent pattern seen from the Table is the seasonal signature, with the higher rainfall occurring in winter months' and lower rainfall in the summer months. (Table 8) gives $\delta D$ and $\delta^{18}O$ values weighted by amount.

**Table 7. UCT rainfall stable isotope data from 1995 to 2016, Collected monthly on the roof of the Department of Geological Sciences, UCT. Data from Harris et al., (2010) and some data unpublished.**

| **Month** | **Year** | **month** | **δD** | **$\delta^{18}$O** | **amount (mm)** | **d-excess** |
|---|---|---|---|---|---|---|
| June | 1995 | 1 | -6 | -3.81 | 120 | 24.39 |
| July | 1995 | 2 | -5 | -2.92 | 297 | 18.36 |
| August | 1995 | 3 | -16 | -4.92 | 138 | 23.45 |
| September | 1995 | 4 | -2 | -2.35 | 67 | 16.70 |
| October | 1995 | 5 | -6 | -3.12 | 160 | 19.16 |
| November | 1995 | 6 | -25 | -4.6 | 18 | 11.80 |
| December | 1995 | 7 | -57 | -8.1 | 15 | 7.80 |
| January | 1996 | 7 | 7 | 1.2 | 4 | -2.60 |
| February | 1996 | 8 | -31 | -4.9 | 50 | 8.00 |
| March | 1996 | 9 | -21 | -5.4 | 56 | 22.22 |
| April | 1996 | 10 | 1 | -2.1 | 85 | 17.30 |
| May | 1996 | 11 | -15 | -5 | 81 | 25.20 |
| June | 1996 | 12 | -7 | -3.5 | 248 | 20.93 |
| July | 1996 | 13 | -19 | -5.9 | 211 | 28.21 |
| August | 1996 | 14 | -22 | -4.97 | 159 | 17.86 |
| September | 1996 | 15 | -11 | -2.98 | 237 | 13.04 |
| October | 1996 | 16 | -2 | -1.87 | 126 | 12.86 |
| November | 1996 | 17 | -16 | -3.35 | 79 | 10.89 |
| December | 1996 | 18 | -15 | -2.57 | 96 | 5.96 |
| January | 1997 | 18 | -11 | -1.39 | 17 | -0.06 |
| February | 1997 | 19 | -1 | -0.43 | 4 | 2.58 |
| March | 1997 | 20 | 4 | -1.37 | 13 | 14.91 |
| April | 1997 | 21 | -11 | -3.41 | 94 | 16.29 |
| May | 1997 | 22 | -24 | -5 | 146 | 16.24 |
| June | 1997 | 23 | -19 | -4.72 | 158 | 19.21 |
| July | 1997 | 24 | -2 | -2.13 | 37 | 14.69 |
| August | 1997 | 25 | -6 | -2.24 | 306 | 12.03 |
| September | 1997 | 26 | -5 | -1.83 | 30 | 9.24 |
| October | 1997 | 27 | -5 | -2.15 | 41 | 12.04 |
| November | 1997 | 28 | -15 | -3.25 | 126 | 10.63 |
| December | 1997 | 29 | 4 | -0.61 | 19 | 8.72 |
| January | 1998 | 29 | -2 | -1.57 | 23 | 10.76 |
| February | 1998 | 30 | 4 | -0.91 | 5 | 11.23 |
| March | 1998 | 31 | -5 | -1.69 | 58 | 8.24 |
| April | 1998 | 32 | -5 | -1.55 | 114 | 7.26 |
| May | 1998 | 33 | -24 | -4.15 | 326 | 9.20 |
| June | 1998 | 34 | -5 | -2.11 | 191 | 12.08 |
| July | 1998 | 35 | -9 | -2.58 | 172 | 11.80 |
| August | 1998 | 36 | -15 | -3.27 | 67 | 11.31 |
| September | 1998 | 37 | -4 | -0.95 | 87 | 3.87 |
| October | 1998 | 38 | -8 | -2.26 | 80 | 9.84 |
| November | 1998 | 39 | -5 | -2.38 | 82 | 14.51 |

| Month | year | month | δD | $\delta^{18}O$ | amount (mm) | d-excess |
|---|---|---|---|---|---|---|
| December | 1998 | 40 | -16 | -2.59 | 52 | 4.69 |
| January | 1999 | 40 | 5 | 0.14 | 15 | 4.09 |
| February | 1999 | 41 | 7 | -0.47 | 13 | 10.54 |
| March | 1999 | 42 | 3 | -1.14 | 5 | 11.86 |
| April | 1999 | 43 | -24 | -5.44 | 79 | 19.04 |
| May | 1999 | 44 | -7 | -2.8 | 125 | 15.70 |
| June | 1999 | 45 | -15 | -3.69 | 169 | 14.28 |
| July | 1999 | 46 | -11 | -3.06 | 159 | 13.97 |
| August | 1999 | 47 | -18 | -4.66 | 253 | 18.92 |
| September | 1999 | 48 | -17 | -4.7 | 246 | 20.30 |
| October | 1999 | 49 | 7 | -0.65 | 5 | 11.84 |
| November | 1999 | 50 | 2 | -1.6 | 58 | 14.92 |
| December | 1999 | 51 | -2 | -1.3 | 4 | 8.53 |
| January | 2000 | 51 | -5 | -2.39 | 39 | 13.94 |
| February | 2000 | 52 | 0 | 0 | 0 | 0.00 |
| March | 2000 | 53 | -32 | -5.59 | 8 | 13.09 |
| April | 2000 | 54 | 3 | -1.23 | 29 | 12.98 |
| May | 2000 | 55 | -4 | -4.24 | 226 | 29.83 |
| June | 2000 | 56 | -15 | -3.13 | 162 | 9.72 |
| July | 2000 | 57 | -14 | -4.71 | 154 | 23.21 |
| August | 2000 | 58 | -8 | -2.65 | 163 | 12.94 |
| September | 2000 | 59 | -3 | -1.98 | 214 | 12.98 |
| October | 2000 | 60 | -1 | -1.16 | 24 | 8.67 |
| November | 2000 | 61 | -11 | -2.54 | 29 | 9.18 |
| December | 2000 | 62 | -2 | -1.64 | 37 | 11.06 |
| January | 2001 | 62 | -13 | -3.45 | 20 | 14.84 |
| February | 2001 | 63 | -2 | -1.2 | 38 | 8.05 |
| March | 2001 | 64 | 0 | 0 | 0 | 0.00 |
| April | 2001 | 65 | -21 | -4.73 | 77 | 17.04 |
| May | 2001 | 66 | -6 | -3.24 | 277 | 19.81 |
| June | 2001 | 67 | -5 | -3.06 | 127 | 19.11 |
| July | 2001 | 68 | -19 | -4.77 | 442 | 19.13 |
| August | 2001 | 69 | -18 | -4.48 | 413 | 17.84 |
| September | 2001 | 70 | -4 | -2.66 | 152 | 17.28 |
| October | 2001 | 71 | 3 | -1.5 | 119 | 15.00 |
| November | 2001 | 72 | -18 | -2.68 | 26 | 3.44 |
| December | 2001 | 73 | 7 | -0.28 | 6 | 9.24 |
| January | 2002 | 73 | -17 | -5.5 | 138 | 27.00 |
| February | 2002 | 74 | 0 | -2.4 | 36 | 19.20 |
| March | 2002 | 75 | 2 | -2.06 | 46 | 18.48 |
| April | 2002 | 76 | 0 | -4.14 | 78 | 33.12 |
| May | 2002 | 77 | 0 | -2.65 | 147 | 21.20 |
| June | 2002 | 78 | -3 | -2.26 | 256 | 15.08 |

| **Month** | **year** | **month** | **δD** | **$\delta^{18}$O** | **amount (mm)** | **d-excess** |
|---|---|---|---|---|---|---|
| July | 2002 | 79 | 0 | -3.39 | 259 | 27.12 |
| August | 2002 | 80 | -36 | -6.43 | 95 | 15.44 |
| September | 2002 | 81 | -14 | -2.99 | 40 | 9.92 |
| October | 2002 | 82 | -15 | -3.85 | 105 | 15.80 |
| November | 2002 | 83 | -9 | -3.31 | 66 | 17.48 |
| December | 2002 | 84 | 18 | 3.47 | 8 | -9.76 |
| January | 2003 | 84 | 18 | 3.3 | 25 | -8.40 |
| February | 2003 | 85 | 11 | 0.28 | 25 | 8.76 |
| March | 2003 | 86 | -22 | -5.6 | 96 | 22.80 |
| April | 2003 | 87 | -3 | -2.3 | 33 | 15.40 |
| May | 2003 | 88 | -7 | -2.7 | 95 | 14.60 |
| June | 2003 | 89 | -5 | -2.9 | 93 | 18.20 |
| July | 2003 | 90 | -16 | -2.71 | 165 | 5.68 |
| August | 2003 | 91 | -23 | -5.04 | 296 | 17.32 |
| September | 2003 | 92 | -12 | -2.76 | 165 | 10.08 |
| October | 2003 | 93 | -4 | -2.18 | 88 | 13.44 |
| November | 2003 | 94 | 9 | -0.66 | 10 | 14.28 |
| December | 2003 | 95 | -1 | -1.45 | 75 | 10.60 |
| January | 2004 | 95 | -18 | -3.55 | 13 | 10.40 |
| February | 2004 | 96 | -10 | -2.87 | 27 | 12.96 |
| March | 2004 | 97 | -8 | -2.75 | 30 | 14.00 |
| April | 2004 | 98 | -15 | -3.54 | 197 | 13.22 |
| May | 2004 | 99 | -6 | -2.79 | 64 | 16.32 |
| June | 2004 | 100 | -21 | -4.65 | 228 | 16.20 |
| July | 2004 | 101 | -14 | -3.47 | 263 | 13.76 |
| August | 2004 | 102 | -10 | -2.67 | 342 | 11.36 |
| September | 2004 | 103 | -10 | -2.38 | 98 | 9.04 |
| October | 2004 | 104 | -31 | -5.67 | 188 | 14.36 |
| November | 2004 | 105 | -4 | -1.51 | 18 | 8.08 |
| December | 2004 | 106 | 5 | -0.5 | 39 | 9.00 |
| January | 2005 | 106 | -7 | -1.94 | 63 | 8.92 |
| February | 2005 | 107 | -4 | -1.4 | 5 | 7.20 |
| March | 2005 | 108 | 0 | -1.16 | 15 | 9.28 |
| April | 2005 | 109 | -37 | -5.37 | 134 | 5.96 |
| May | 2005 | 110 | -26 | -3.22 | 309 | -0.24 |
| June | 2005 | 111 | -14 | -3.15 | 321 | 11.20 |
| July | 2005 | 112 | -14 | -1.67 | 187 | -0.64 |
| August | 2005 | 113 | -15 | -3.13 | 287 | 10.04 |
| September | 2005 | 114 | -6 | -2.4 | 98 | 13.20 |
| October | 2005 | 115 | 1 | 0 | 55 | 1.00 |
| November | 2005 | 116 | 4 | 0.97 | 23 | -3.76 |
| December | 2005 | 117 | 0 | 0 | 0 | 0.00 |
| January | 2006 | 117 | 0 | 0 | 0 | 0.00 |

| **Month** | **year** | **month** | **δD** | **$\delta^{18}$O** | **amount (mm)** | **d-excess** |
|---|---|---|---|---|---|---|
| February | 2006 | 118 | -3 | -1.71 | 60 | 10.68 |
| March | 2006 | 119 | -4 | -1.5 | 17 | 8.00 |
| April | 2006 | 120 | -18 | -3.83 | 85 | 12.64 |
| May | 2006 | 121 | -18 | -3.4 | 289 | 9.20 |
| June | 2006 | 122 | -13 | -3.02 | 117 | 11.16 |
| July | 2006 | 123 | -11 | -2.74 | 251 | 10.92 |
| August | 2006 | 124 | -14 | -2.91 | 213 | 9.28 |
| September | 2006 | 125 | -15 | -2.6 | 76 | 5.80 |
| October | 2006 | 126 | -7 | -2.18 | 86 | 10.44 |
| November | 2006 | 127 | -24 | -4.38 | 112 | 11.04 |
| December | 2006 | 128 | -9 | -2.42 | 30 | 10.36 |
| January | 2007 | 128 | 11 | 1.27 | 27 | 0.84 |
| February | 2007 | 129 | 0 | -3.03 | 46 | 24.24 |
| March | 2007 | 130 | -3 | -2.82 | 49 | 19.56 |
| April | 2007 | 131 | -2 | -2.72 | 156 | 19.76 |
| May | 2007 | 132 | -14 | -3.36 | 162 | 12.88 |
| June | 2007 | 133 | -22 | -4.62 | 353 | 14.96 |
| July | 2007 | 134 | -15 | -3.66 | 334 | 14.28 |
| August | 2007 | 135 | -21 | -4.06 | 229 | 11.48 |
| September | 2007 | 136 | -2 | -1.84 | 115 | 12.72 |
| October | 2007 | 137 | 0 | -3.58 | 46 | 28.64 |
| November | 2007 | 138 | -4 | -1.66 | 177 | 9.28 |
| December | 2007 | 139 | 11.3 | 1.52 | 40 | -0.85 |
| January | 2008 | 139 | -1.4 | -2.40 | 30 | 17.83 |
| February | 2008 | 140 | 13.9 | -1.22 | 43 | 23.61 |
| March | 2008 | 141 | -6.6 | -2.23 | 10 | 11.26 |
| April | 2008 | 142 | -7.3 | -2.66 | 20 | 13.97 |
| May | 2008 | 143 | 0.5 | -1.78 | 224 | 14.72 |
| June | 2008 | 144 | -13.3 | -3.27 | 262 | 12.79 |
| July | 2008 | 145 | -14.8 | -4.66 | 358 | 22.47 |
| August | 2008 | 146 | -24.8 | -4.03 | 262 | 7.43 |
| September | 2008 | 147 | -16.3 | -3.07 | 337 | 8.26 |
| October | 2008 | 148 | -1.1 | -1.87 | 47 | 13.87 |
| November | 2008 | 149 | -16.0 | -3.61 | 52 | 12.80 |
| December | 2008 | 150 | -2.0 | -0.9 | 38 | 5.20 |
| January | 2009 | 164 | -3 | -0.30 | 3 | -0.52 |
| February | 2009 | 165 | -4 | -0.28 | 14 | -1.51 |
| March | 2009 | 166 | 7 | 2.03 | 5 | -9.13 |
| April | 2009 | 167 | -5 | -1.88 | 72 | 10.26 |
| May | 2009 | 168 | -10 | -3.25 | 220 | 15.87 |
| June | 2009 | 169 | -13 | -2.71 | 393 | 8.48 |
| July | 2009 | 170 | -23 | -4.53 | 220 | 13.66 |
| August | 2009 | 171 | -23 | -4.50 | 393 | 12.80 |

| **Month** | **year** | **month** | **δD** | **$\delta^{18}O$** | **amount (mm)** | **d-excess** |
|---|---|---|---|---|---|---|
| September | 2009 | 172 | -8 | -2.21 | 169 | 9.61 |
| October | 2009 | 173 | -17 | -3.16 | 76 | 8.52 |
| November | 2009 | 174 | -32 | -5.09 | 185 | 8.72 |
| December | 2009 | 175 | -1 | -0.56 | 16 | 3.75 |
| January | 2010 | 176 | 10 | 0.75 | 9 | 3.63 |
| February | 2010 | 177 | -6 | -0.54 | 12 | -1.50 |
| March | 2010 | 178 | 0 | -0.83 | 7 | 7.06 |
| April | 2010 | 179 | -12 | -2.25 | 44 | 5.93 |
| May | 2010 | 180 | -8 | -2.78 | 277 | 13.88 |
| June | 2010 | 181 | -17 | -3.31 | 222 | 9.45 |
| July | 2010 | 182 | -15 | -3.69 | 166 | 14.45 |
| August | 2010 | 183 | -5 | -1.74 | 121 | 8.99 |
| September | 2010 | 184 | -3 | -2.24 | 100 | 14.59 |
| October | 2010 | 185 | -3 | -2.15 | 102 | 13.91 |
| November | 2010 | 186 | -6 | -2.39 | 73 | 12.95 |
| December | 2010 | 187 | -40 | -5.06 | 17 | 0.52 |
| January | 2011 | 188 | -5 | -0.15 | 16 | -4.04 |
| February | 2011 | 189 | 14 | 3.19 | 3 | -11.56 |
| March | 2011 | 190 | -24 | -4.12 | 16 | 9.34 |
| April | 2011 | 191 | -6 | -2.73 | 111 | 16.11 |
| May | 2011 | 192 | -12 | -3.69 | 145 | 17.16 |
| June | 2011 | 193 | -18 | -4.82 | 191 | 20.20 |
| July | 2011 | 194 | -15 | -4.68 | 49 | 22.85 |
| August | 2011 | 195 | -4 | -2.63 | 209 | 17.18 |
| September | 2011 | 196 | 0 | -1.51 | 141 | 11.97 |
| October | 2011 | 197 | -17 | -3.48 | 41 | 10.80 |
| November | 2011 | 198 | -12 | -3.21 | 72 | 13.67 |
| December | 2011 | 199 | -1.60 | -2.05 | 62 | 14.78 |
| January | 2012 | 200 | 5 | 0.78 | 46 | -0.84 |
| February | 2012 | 201 | -2 | -0.68 | 21 | 2.95 |
| March | 2012 | 202 | -12 | -3.07 | 69 | 12.64 |
| April | 2012 | 203 | -9.79 | -3.12 | 133 | 15.13 |
| May | 2012 | 204 | -10.40 | -3.08 | 143 | 14.24 |
| June | 2012 | 205 | -6.38 | -4.15 | 226 | 26.80 |
| July | 2012 | 206 | -8.80 | -2.67 | 293 | 12.56 |
| August | 2012 | 207 | -13.55 | -3.25 | 214 | 12.48 |
| September | 2012 | 208 | -10.76 | -2.36 | 172 | 8.15 |
| October | 2012 | 209 | -7.05 | -3.16 | 44 | 18.20 |
| November | 2012 | 210 | 0.9 | -1.13 | 59.5 | 9.95 |
| December | 2012 | 211 | 7.2 | -0.21 | 9 | 8.87 |
| January | 2013 | 212 | 0.36 | -2.04 | 25.8 | 16.69 |
| February | 2013 | 213 | 3.00 | -1.12 | 54.5 | 11.96 |

| **Month** | **year** | **month** | **δD** | **$\delta^{18}$O** | **amount (mm)** | **d-excess** |
|---|---|---|---|---|---|---|
| March | 2013 | 214 | -8.60 | -1.13 | 75.6 | 0.43 |
| April | 2013 | 215 | -17.36 | -2.81 | 186 | 5.12 |
| May | 2013 | 216 | -4.59 | -2.07 | 231.3 | 11.95 |
| June | 2013 | 217 | -18.33 | -4.09 | 347.4 | 14.36 |
| July | 2013 | 218 | -4.58 | -1.43 | 184.5 | 6.87 |
| August | 2013 | 219 | -23.27 | -5.16 | 421.6 | 18.01 |
| September | 2013 | 220 | -8.17 | -2.68 | 237.8 | 13.28 |
| October | 2013 | 221 | -10.33 | -2.85 | 89.9 | 12.49 |
| November | 2013 | 222 | -26.13 | -3.87 | 128.8 | 4.85 |
| December | 2013 | 223 | 12.69 | 1.56 | 12.5 | 0.25 |
| January | 2014 | 224 | -4.03 | -2.36 | 49.3 | 14.87 |
| February | 2014 | 225 | 12.68 | 2.32 | 16 | -5.90 |
| March | 2014 | 226 | -8.01 | -2.84 | 157.8 | 14.74 |
| April | 2014 | 227 | -13.47 | -4.46 | 54.3 | 22.20 |
| May | 2014 | 228 | -2.54 | -2.27 | 92.5 | 15.64 |
| June | 2014 | 229 | -9.53 | -3.53 | 274.2 | 18.75 |
| July | 2014 | 230 | -12.56 | -4.05 | 243.2 | 19.81 |
| August | 2014 | 231 | -13.02 | -3.54 | 212.2 | 15.33 |
| September | 2014 | 232 | -10.76 | -3.31 | 43.4 | 15.75 |
| October | 2014 | 234 | -3.83 | -3.04 | 6.5 | 20.52 |
| November | 2014 | 235 | -1.67 | -3.11 | 58.7 | 23.21 |
| December | 2014 | 236 | 6.09 | -0.25 | 32.7 | 8.08 |
| January | 2015 | 237 | 0.57 | -1.58 | 67 | 13.22 |
| February | 2015 | 238 | 12.66 | 0.32 | 23 | 10.06 |
| March | 2015 | 239 | 11.61 | 0.27 | 6.3 | 9.41 |
| April | 2015 | 240 | -5.25 | -2.97 | 18 | 18.50 |
| May | 2015 | 241 | -5.51 | -1.75 | 84.9 | 8.53 |
| June | 2015 | 242 | -5.33 | -3.76 | 293 | 24.74 |
| July | 2015 | 243 | -15.51 | -3.85 | 187.4 | 15.28 |
| August | 2015 | 245 | 0.42 | -1.42 | 93.5 | 11.79 |
| September | 2015 | 246 | -1.81 | -1.69 | 101.4 | 11.70 |
| October | 2015 | 247 | -6.23 | -3.10 | 91 | 18.57 |
| November | 2015 | 248 | -0.10 | -1.70 | 24.2 | 13.50 |
| December | 2015 | 249 | 13.80 | 1.70 | 16.7 | 0.20 |
| January | 2016 | 250 | -1.20 | -2.25 | 61 | 16.80 |
| February | 2016 | 251 | -13.10 | -1.52 | 2.7 | -0.94 |
| March | 2016 | 252 | -6.00 | -2.93 | 72 | 17.44 |
| April | 2016 | 253 | -3.80 | -2.03 | 152 | 12.44 |
| May | 2016 | 254 | -4.30 | -3.02 | 43.5 | 19.86 |
| June | 2016 | 255 | -4.80 | -2.83 | 254.5 | 17.84 |
| July | 2016 | 256 | -28.93 | -5.24 | 234.3 | 12.99 |
| August | 2016 | 257 | -17.76 | -3.19 | 121 | 7.76 |
| September | 2016 | 258 | -6.70 | -2.90 | 90 | 16.50 |

| Month | year | month | δD | $\delta^{18}O$ | amount (mm) | d-excess |
|---|---|---|---|---|---|---|
| October | 2016 | 259 | -2.64 | -0.80 | 34 | 3.76 |
| November | 2016 | 260 | 5.72 | 0.94 | 12 | -1.80 |
| December | 2016 | 261 | 8.14 | -0.10 | 111 | 8.94 |

### 4.2.1 Rainfall Amount

The monthly rainfall samples were used to calculate the annual amount and the mean and weighted mean (δ values weighted by amount). The monthly rainfall amount is presented in (Table 7), this represents the monthly UCT rainfall collected from 1995 to 2016.The annual amount variation is evident (mm) in (Table 8), with 2013 receiving the highest annual rainfall with the amount of 1978 mm and 1997 receiving the least annual rainfall amount of 992 mm. The year of 1995 only 6 months of this particular year was sampled; the data from that year is not included in the table. Long-term data of the rain is important for a study on the long-term trends for a number of studies in the Earth and life sciences.

**Table 8. Weighted annual δD and $\delta^{18}O$ rainfall from 1996 to 2006.**

| Year | Total annual rainfall amount (mm) | Weighted δD (‰) | Weighted $\delta^{18}O$ (‰) |
|---|---|---|---|
| 1996 | 1432 | -12.98 | -3.83 |
| 1997 | 992 | -11.80 | -3.19 |
| 1998 | 1256 | -11.42 | -2.65 |
| 1999 | 1131 | -13.77 | -3.83 |
| 2000 | 1085 | -7.71 | -3.11 |
| 2001 | 1697 | -12.25 | -3.76 |
| 2002 | 1274 | -7.08 | -3.48 |
| 2003 | 1166 | -12.34 | -3.22 |
| 2004 | 1506 | -15.05 | -3.53 |
| 2005 | 1495 | -16.89 | -2.87 |
| 2006 | 1334 | -14.19 | -3.03 |
| 2007 | 1733 | -11.82 | -3.23 |
| 2008 | 1683 | -12.66 | -3.28 |
| 2009 | 1766 | -17.23 | -3.53 |
| 2010 | 1150 | -10.00 | -2.73 |
| 2011 | 1056 | -9.03 | -3.13 |
| 2012 | 1430 | -8.66 | -2.85 |
| 2013 | 1978 | -13.96 | -3.22 |
| 2014 | 1240.8 | -8.90 | -3.25 |
| 2015 | 1006.4 | -5.08 | -2.70 |
| 2016 | 1188 | -9.41 | -2.87 |

Although there is rainfall data dating back to 1995 only the monthly rainfall amount data from 2013 to 2016 is presented in (Figure 20), this mark the time the studied springs were sampled on a monthly basis. The graph shows the difference in rainfall pattern from one year to other. 2013 received much more rainfall than subsequent three years. The rainfall is presented as monthly amounts and some of the notable variations in the season, high rainfall from April to September and low rainfall from October to March. For example, in the year 2016 during the high rainfall season, June received the highest amount of rainfall of 245.5 mm and during the low rainfall season November received the lowest amount of the year of 12 mm. Seasonality is evident with a general decrease of rainfall during the summer months, while the winter months receive more rainfall. This is a typical winter rainfall pattern for the Western Cape Province (Mediterranean climate), high rainfall, and the rest of the country receiving low rainfall amount. There is a negative relationship between temperature and rainfall amount (Figure 11), the months with high temperatures received the least rainfall.

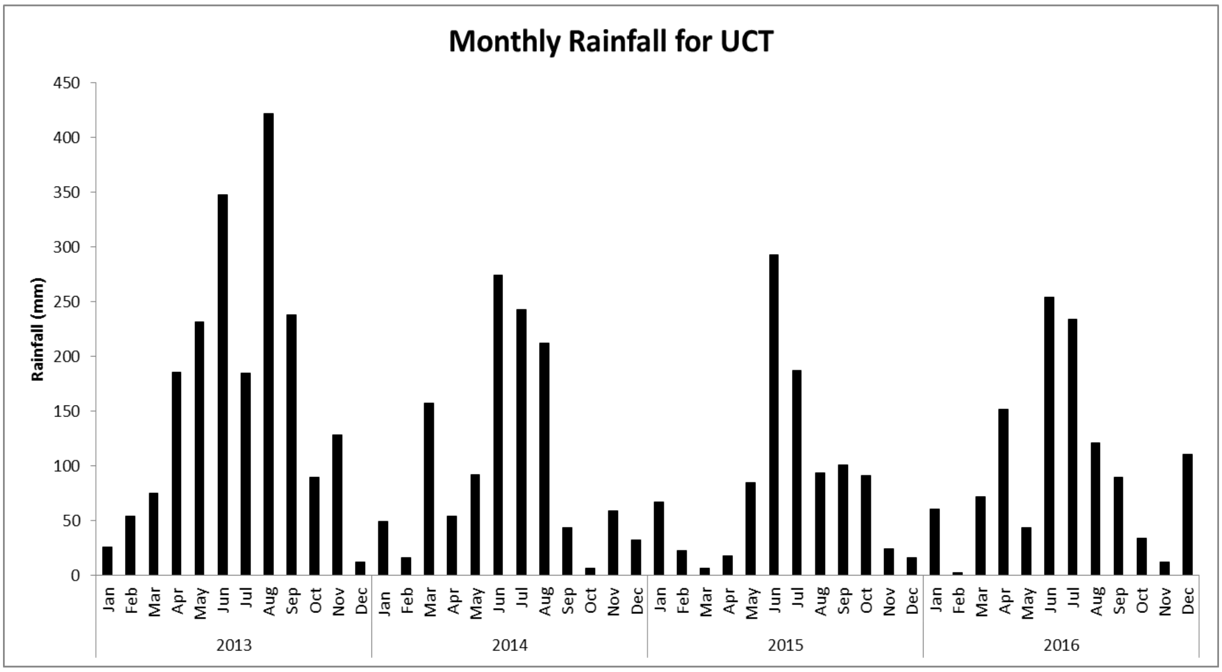


**Figure 20. Plot of the monthly amount of rainfall (mm) for the sampled collected at UCT from 2013 to 2016.**

## 4.3 Rainfall Isotopes

The isotopic composition of the rainfall, the deuterium excess values, and the monthly precipitation amount are reported in (Table 7). The long-term variation in isotope composition of rainfall will be used to estimate the recharge rate of the springs. The rainfall isotope composition is important because the isotope signature behaviour as a tracer, variation with the rainfall isotope composition will be compared with the variation in the springs' isotope composition.

### 4.3.1 Temporal variations - δD and $\delta^{18}O$ isotopic composition of the rainfall

Figure 21 is a plot of rainfall δD and $\delta^{18}O$ values, monthly amounts, and monthly average temperatures. From the diagram, the isotope values seem to have the same pattern from year to year with a few outliers. There is a general pattern standing out of, lower δD and $\delta^{18}O$ values with an increase in rainfall amount, and then there are occasional spikes in δD and $\delta^{18}O$ values, especially with the δD values. The rainfall amounts are variable, seasonality changes, and the δD and $\delta^{18}O$ values of the rainfall also varies with the amount. The variation in δD and $\delta^{18}O$ with the monthly amount and clearly depict some of the variation is seasonal with higher values in summer months and lower values in winter months. There is a negative correlation between the amount of rainfall with δD and $\delta^{18}O$ values. There is a pattern of more negative δD and $\delta^{18}O$ values over winter months (high rainfall) and more positive δD and $\delta^{18}O$ values over summer months (low rainfall), for both δD and δ$^{18}$O, this pattern is evident from year to year. This data represent the isotopic composition of the rain collected for the past 21 years. The dataset with a range of δD and δ$^{18}$O values from -57 to 18 ‰ and -8.1 to 3.19 ‰, respectively. Most δD and δ$^{18}$O values are between -60 and -20‰, and -10 and 4‰, respectively.

The correlation coefficient between δD and amount is -0.42 and between δ$^{18}$O is -0.49. The temperature effect and the amount effect were discussed in chapter 1; there seem to be a temperature effect, and amount effect evident in this dataset. From the diagram when the temperatures are low, the δD and δ$^{18}$O values are lighter. During winter months when the temperature is lower and the rainfall amount is higher, the rainfall had low δD and δ$^{18}$O values. During the summer months, the pattern is reversed; the temperature is warmer and the rainfall amount is lower, resulting in less negative δD and δ$^{18}$O values. This is because as the amount of rainfall increase, the heavy isotopes are removed from the rainfall faster and therefore the rainfall has lighter isotopes and the opposite for decrease in rainfall amount. Dansgaard (1964) was the first author to point out that variations in the stable isotope composition of rainfall depend on many factors, and these include; rainfall amount, temperature, moisture source, and meteorological conditions (evaporation, condensation, altitude, and precipitation).The resulting pattern for this dataset seems to stem from the temperature effect and amount effect; in winter, temperatures are colder and rainfall amounts are greater, so rainout removes heavier isotopes faster and the lighter isotopes become more abundant in the rain, resulting in more negative δD and δ$^{18}$O values. In summer the reverse is true; rainfall amounts are lesser and temperatures are warmer, resulting in less negative δD and δ$^{18}$O values. The relationship between δD and δ$^{18}$O in precipitation is defined as a meteoric water line (MWL).

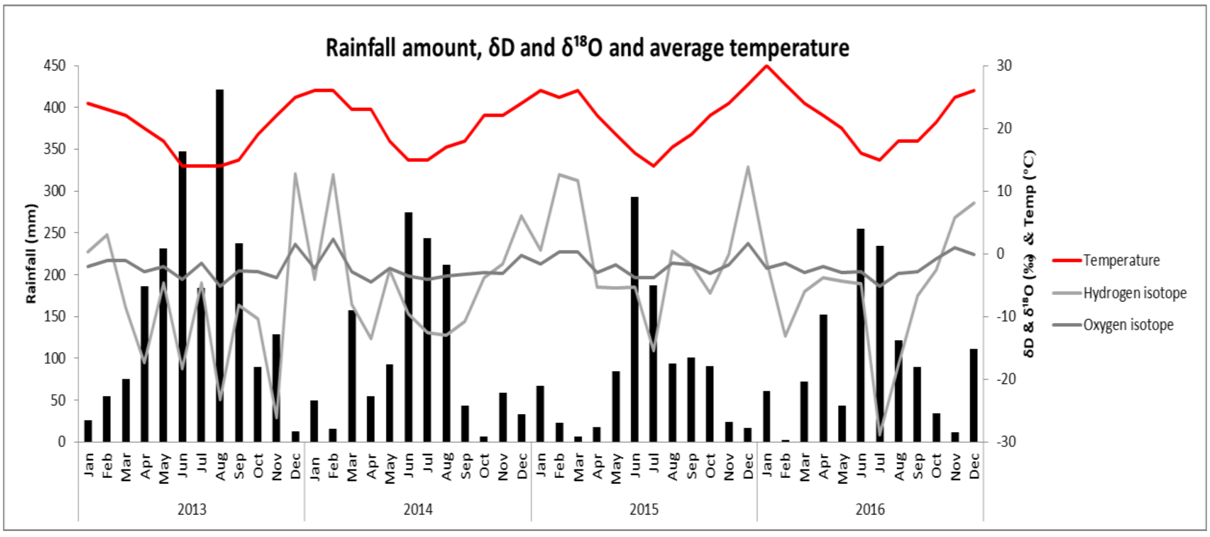


**Figure 21. Plot of rainfall amount, rainfall δD, δ$^{18}$O and the average temperature.**

### 4.3.2 Arithmetic means and Weighted means

Mean annual δD and δ$^{18}$O values for rainfall can be calculated in two ways; (i) a simple arithmetic mean, and (ii) a weighted mean, weighted according to the rainfall amount for each month. Weighted annual δD and δ$^{18}$O values reflect recharge values better than arithmetic means. The results demonstrate two significant patterns. The monthly samples mean δD and δ$^{18}$O values are typically more variable and less negative than the weighted annual δD and δ$^{18}$O values (Figure 22), the annual weighted means is presented in (Table 8).The weighted annual mean δD and δ$^{18}$O range from -16.89‰ to -5.08‰ and -3.83‰ to -2.65‰, respectively. The weighted annual mean has a lower δD and δ$^{18}$O value than the arithmetic mean. This is because the less negative values are associated with low rainfall events, during summer months where temperatures are higher and isotope values of rain are less negative and evaporation further increases the isotope values, the amount affect (Dansgaard, 1964). On the other hand, the high rainfall, cold and isotopically more depleted winter rainfall bring the weighted means down towards more negative isotope values.

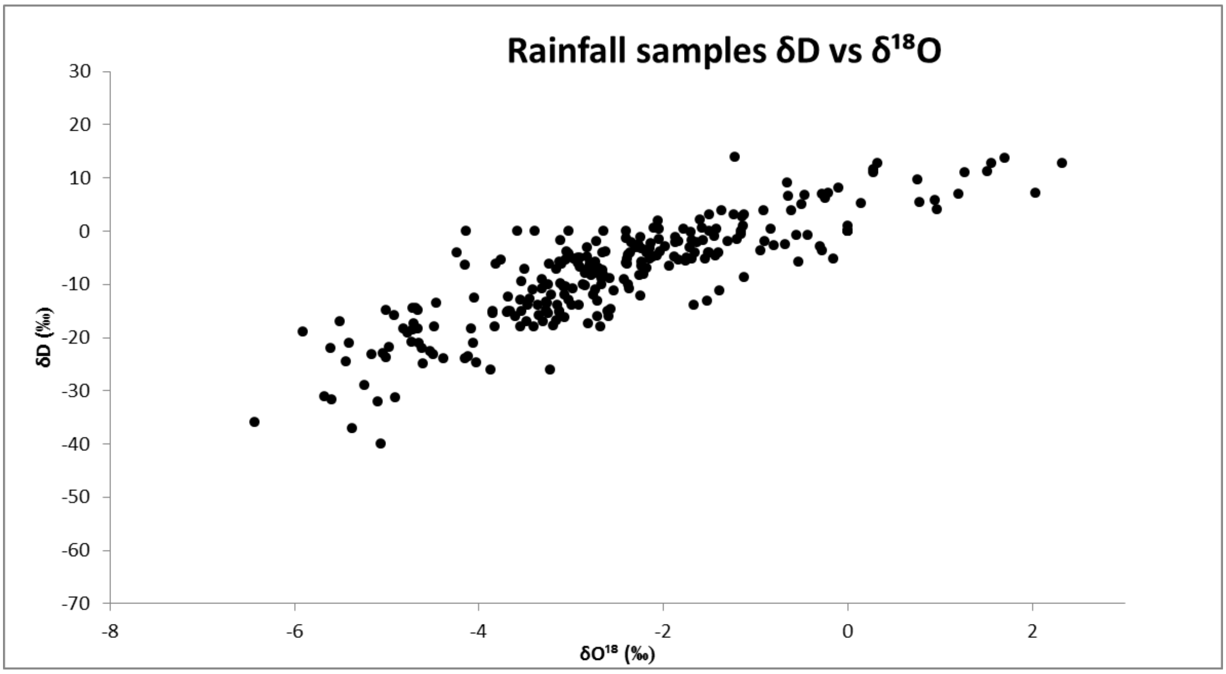


**Figure 22. Plot of δD vs δ$^{18}$O for UCT monthly samples from 1995 to 2016.**

### 4.3.3 Local Meteoric Water Lines

The line of best fit through δD vs δ$^{18}$O array (Figure 23) was calculated using the reduced major axis method (RMA). (RMA) is used when both variables are dependent and no variable is more certain than the other. The (RMA) assumes that there are errors to both y and x values, in this case both the δD and δ$^{18}$O data. The local meteoric water line specific to a location is controlled by local factors specific to the climate of that local, this includes evaporation of the precipitation, storms characteristic of the area and the oceanic origin of the water vapour. Such local factors work together to produce the slope and d-excess specific to that LMWL. The most noticeable feature of this graph is the well-defined correlation between δD and δ$^{18}$O. The correlation coefficient between the rainfall δD and δ$^{18}$O values is ($r = 0.92$). The line of the best fit is the local meteoric water line. The dataset was used to plot and calculate lines of best fit (local meteoric water lines) the equations are as follows: rainfall data: $\delta D = 6.03*\delta^{18}O + 7.07$. The equation of the line best fit is similar to the line of best fit calculated by Harris et al. (2010) which was $\delta D = 6.41*\delta^{18}O + 8.66$. The line of best fit is less steep than global meteoric water line (GMWL). In the diagram of δD and δ$^{18}$O, most of the samples lie above the global meteoric water line (GMWL) (Figure 23). The slope of the LMWL is slightly less steep than the GMWL. The bulk of the outliers represent small monthly amounts that could have evaporated (both in the air and in the collector).

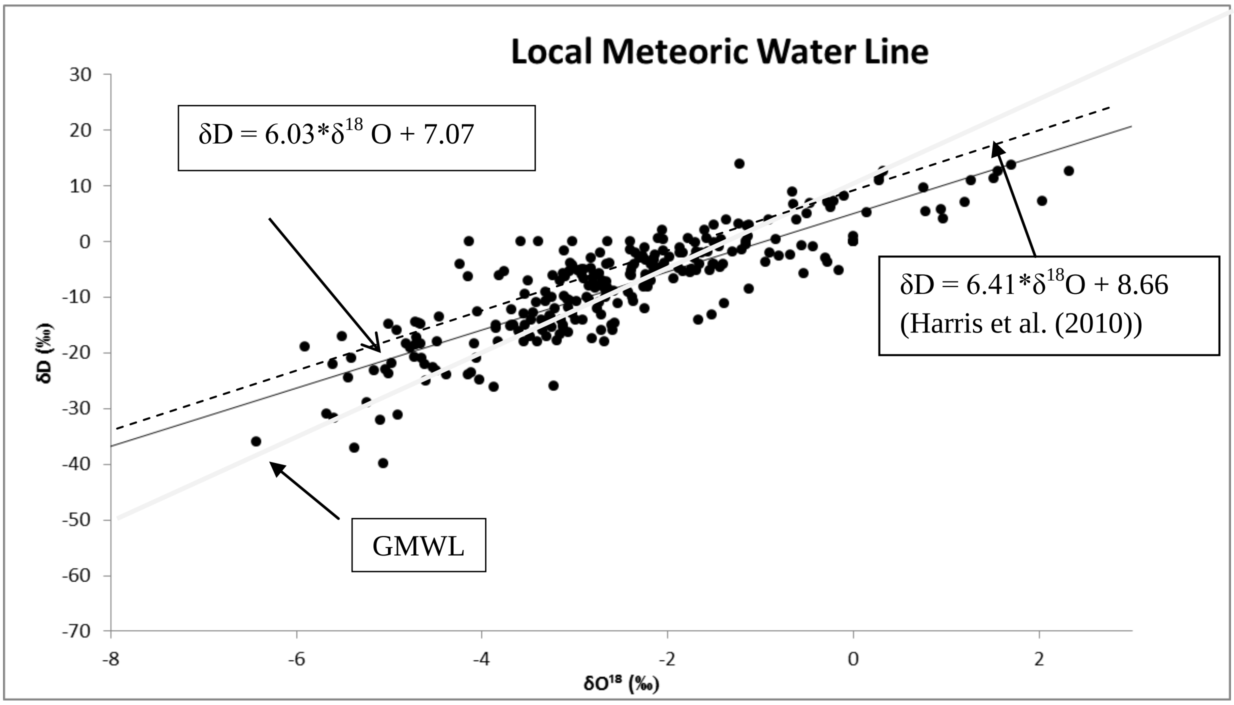


**Figure 23. Plot of δD and $\delta^{18}$O for UCT monthly samples from 1995-2016. The line of the best fit through the data (local meteoric water line) was calculated using the reduced major axis method. Also show on the graph is the best fit line calculated by Harris et al. (2010) with monthly samples from 1996-2008.**

### 4.3.4 Deuterium Excess

The deuterium excess is a useful way of describing the variation of composition of water on a δD versus $\delta^{18}$O diagram. The d-excess was calculated for each of the results to identify data outliers and to compare with the normally expected global range of d-excess values (Table 7). Global meteoric water line (GMWL) has the equation $\delta D = 8*d\delta^{18}O + 10$. The d refers to an individual rain sample, and the d-excess is calculated for a known sample δD and $\delta^{18}$O values by the equation d-excess= $\delta D - 8*\delta^{18}O$. The d-excess values for the rainfall samples range from -11.56 to 33.12 and average of 11.19, which is similar to d-excess values from other studies in Mediterranean climates. The d-excess appears to be mostly the same (± 15), but with occasional low values. The d-excess varies between summer and winter, the d-excess values seem to be higher during the winter months and lower during the summer months, see (Figure 24). Negrel et al. (2011) wrote that d-excess values that are less than 5, suggest significant evaporation of the rainwater. This rainfall dataset has got an average d-excess amount of 11.19; the rainfall does not seem to have been significantly impacted by evaporation, with d-excess values mostly above 5.The d-excess reflect meteorological condition, which is the impact of evaporation. The correlation coefficient between d-excess and the monthly rainfall amount is a relatively weak positive correlation of (r = 0.34). (Figure 24) also include a plot of the d-excess values and the average temperature. The d-excess decreases with an increase in temperature, the correlation coefficient between the two variables is a negative correlation of (r = –0.37), a pattern of low d-excess when temperature is high. So in the Western Cape Province during the summer months when the temperatures increase and an amount of rainfall decreases, the d-excess values are low.

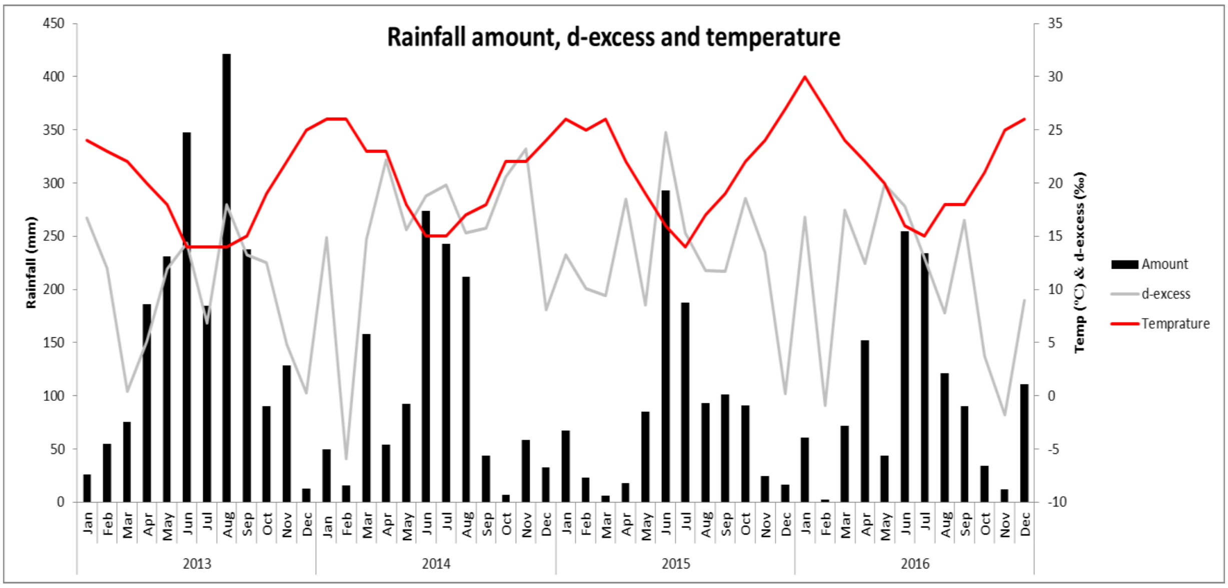


**Figure 24. Plot of rainfall amount, d-excess and average temperature.**

## 4.4 Springs

This section will report the isotope data and the hydrochemistry data of the four investigated springs. The four springs were initially sporadically sampled from 1996 to 2013; from 2014 the springs were sampled on a monthly base. All the springs' isotope data from 2013 to 2016 is presented in (Table 9). The isotope compositions of the springs are a useful tool for calculating recharge rate and tracing the flow pattern of the groundwater. The temperature and EC of the springs sample water were also measured; this was for monitoring the water quality.

**Table 9. Springs stable isotope data from 2013-2016.**

| Springs | Albion | | De Waal | | Main-spring | | Newlands | |
|---|---|---|---|---|---|---|---|---|
| (‰) | $\delta D$ | $\delta^{18}O$ | $\delta D$ | $\delta^{18}O$ | $\delta D$ | $\delta^{18}O$ | $\delta D$ | $\delta^{18}O$ |
| 2013 | -7.72 | -2.71 | -5.50 | -1.49 | -9.00 | -3.51 | -7.00 | -2.72 |
| | -8.05 | -2.17 | -5.30 | -1.56 | -12.10 | -2.85 | -9.80 | -2.37 |
| 2014 | -7.90 | -2.10 | -5.90 | -1.70 | -12.10 | -3.00 | -9.30 | -2.50 |
| | -7.30 | -2.80 | -5.90 | -2.30 | -10.60 | -3.70 | -9.10 | -3.30 |
| | -8.70 | -2.80 | -5.00 | -2.30 | -10.50 | -3.60 | -6.90 | -3.30 |
| | -7.50 | -2.90 | -6.90 | -2.40 | -12.40 | -3.60 | -8.30 | -3.00 |
| | -6.30 | -2.80 | -4.50 | -2.10 | -11.70 | -3.70 | -8.20 | -3.00 |
| | -5.60 | -2.60 | -6.00 | -2.40 | -10.50 | -3.60 | -6.30 | -3.00 |
| | -6.00 | -2.70 | -5.90 | -2.50 | -10.30 | -3.60 | -7.50 | -3.40 |
| | -6.60 | -2.90 | -5.30 | -2.60 | -9.90 | -3.50 | -7.30 | -3.00 |
| | -2.80 | -3.02 | -2.90 | -3.73 | -4.57 | -3.50 | -2.80 | -3.85 |
| | -9.40 | -2.58 | -9.10 | -2.25 | -11.30 | -3.42 | -9.40 | -3.09 |
| 2015 | -8.40 | -2.66 | -6.70 | -2.47 | -13.60 | -3.44 | -9.80 | -2.98 |
| | -8.90 | -3.55 | -6.30 | -2.31 | -14.80 | -3.52 | -9.50 | -3.48 |
| | -7.40 | -2.99 | -10.20 | -2.55 | -14.10 | -3.82 | -9.00 | -3.13 |
| | -6.90 | -2.17 | -9.40 | -2.41 | -12.00 | -3.62 | -6.30 | -3.11 |
| | -8.40 | -2.97 | -8.60 | -2.66 | -13.30 | -4.06 | -6.90 | -3.34 |
| | -11.50 | -2.89 | -11.30 | -4.30 | -13.30 | -4.70 | -10.10 | -3.09 |
| | -8.20 | -3.55 | -12.30 | -3.15 | -14.30 | -4.51 | -11.70 | -3.27 |
| | -10.60 | -3.55 | -10.60 | -3.59 | -13.90 | -2.85 | -11.00 | -4.79 |
| | -10.20 | -2.72 | -8.20 | -3.04 | -13.50 | -3.26 | -12.30 | -3.01 |
| | -9.10 | -2.55 | -9.10 | -2.98 | -12.30 | -3.80 | -9.50 | -3.09 |
| | -9.00 | -4.52 | -7.90 | -3.16 | -13.00 | -2.82 | -10.40 | -3.70 |
| | -7.90 | -2.50 | -4.90 | -3.70 | -10.30 | -2.81 | -6.80 | -3.68 |
| 2016 | -8.40 | -2.87 | -7.70 | -2.61 | -11.90 | -3.34 | -10.10 | -2.61 |
| | -7.60 | -2.74 | -3.90 | -2.41 | -9.90 | -3.41 | -7.60 | -3.43 |
| | -5.80 | -3.09 | -5.10 | -2.41 | -9.90 | -3.69 | -5.70 | -3.08 |
| | -6.40 | -2.76 | -3.90 | -2.54 | -10.50 | -3.60 | -7.50 | -3.47 |
| | -7.00 | -2.82 | -4.90 | -2.01 | -11.40 | -3.44 | -8.10 | -3.26 |
| | -7.00 | -2.92 | -4.10 | -2.54 | -7.70 | -4.10 | -7.30 | -2.92 |
| | -7.31 | -2.04 | -7.01 | -2.28 | -13.69 | -3.78 | -9.91 | -3.03 |
| | -10.40 | -2.92 | -4.31 | -1.65 | -10.90 | -3.22 | -10.12 | -3.16 |
| | -10.52 | -2.90 | -5.87 | -2.08 | -11.56 | -3.27 | -9.14 | -2.97 |
| | -9.20 | -2.97 | -6.66 | -2.26 | -12.88 | -3.59 | -10.07 | -3.17 |
| | -6.33 | -1.76 | -3.02 | -1.58 | -10.92 | -2.95 | -6.31 | -2.30 |
| | -0.87 | -0.13 | -3.17 | -0.71 | -10.02 | -2.23 | -8.47 | -2.32 |

### 4.2.1 Hydrochemical Characteristics of the springs’

The hydrochemical characteristics of the springs’ water were investigated. The aim was to detect if there were correlations between the EC values with the temperature and isotopic signature of the springs. The EC and temperature of the spring waters were measured and recorded on site during sampling, data in (Table 10). The temperature readings can give an indication of whether the water is influenced by surface temperatures or whether the groundwater has travelled to great depths before being discharged as spring water. There are small changes in temperature in different springs and during different seasons, the lowest temperature recorded was 15.4 ºC and the highest 21.3 ºC. The seasonal temperature ranges show consistency with the actual surface temperatures (Figure 25) for particular season suggesting that the aquifer is not far from the surface, but some of the water was not sampled at the source of these springs and probably temperatures were increased or decreased when reaching the outlet point before sampling. Some springs were directed by PVC pipe to a destined outlet. The springs’ temperature shows slight increase and decrease at the surface temperatures increase and decrease.

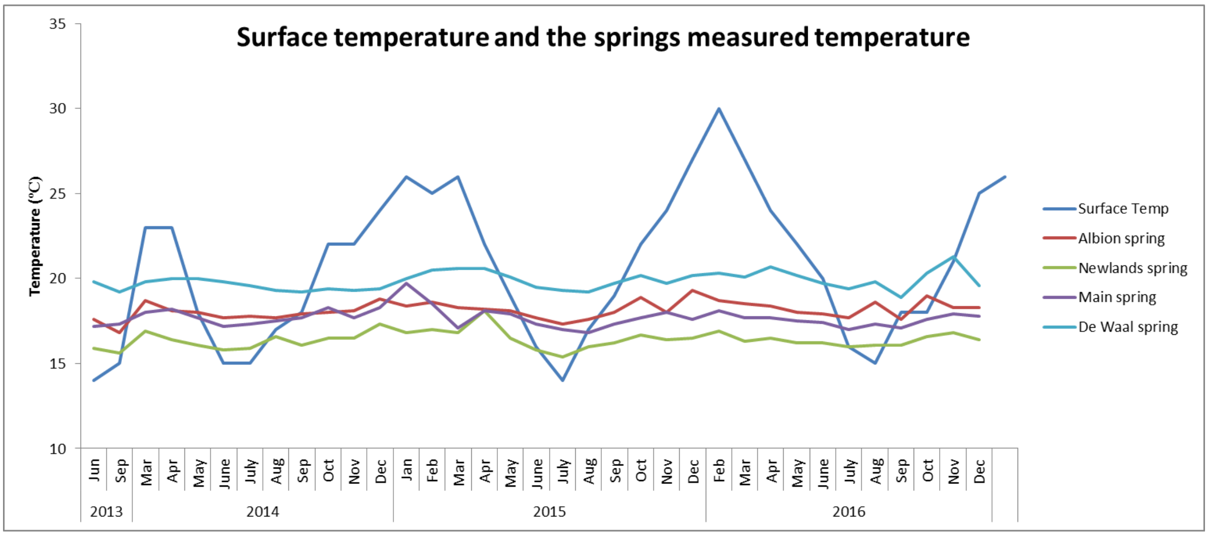


**Figure 25**. **Surface temperature and the springs’ measured average temperature.**

On the other hand, the springs with high yields can maintain the temperature of the water, springs with large yield i.e. Main spring, Newlands spring and Albion spring are unlikely to change that much when the surface temperature changes. (Table 11) show each spring’s daily yields and the springs’ average temperatures. The table shows no relationship between the springs’ yield and the springs’ average temperature. Albion spring had the highest yield and the second highest average temperature, while De Waal spring has got the lowest yield but has the highest temperature.

**Table 10. Springs daily yields and average spring temperature.**

| Springs | Yields (l/day) | Average spring temp (ºC) |
|---|---|---|
| Main spring | 2.2x10$^{6}$ | 17.7 |
| De Waal | 1.4x10$^{6}$ | 19.8 |
| Albion | 3.0x10$^{6}$ | 18.1 |
| Newlands | 1.55x10$^{6}$ | 16.4 |

**Table 11. Hydrochemical characteristics of the springs' water.**

| | | Albion | | Newlands | | Main spring | | De Waal | |
|---|---|---|---|---|---|---|---|---|---|
| Year | Month | EC (µS/cm) | Temp (ºC) | EC (µS/cm) | Temp (ºC) | EC (µS/cm) | Temp (ºC) | EC (µS/cm) | Temp (ºC) |
| 2013 | Jun | 210 | 17.6 | 132.6 | 15.9 | 183.3 | 17.2 | 167.7 | 19.8 |
| | Sep | 220 | 16.8 | 130.9 | 15.6 | 159.3 | 17.3 | 176.6 | 19.2 |
| 2014 | Mar | 212 | 18.7 | 132.2 | 16.9 | 182.5 | 18 | 173.2 | 19.8 |
| | Apr | 211 | 18.1 | 128.7 | 16.4 | 174.7 | 18.2 | 171.5 | 20 |
| | May | 212 | 18 | 128.4 | 16.1 | 181 | 17.7 | 172.2 | 20 |
| | June | 212 | 17.7 | 131.8 | 15.8 | 163.1 | 17.2 | 169.5 | 19.8 |
| | July | 213 | 17.8 | 131.2 | 15.9 | 151.5 | 17.3 | 172.6 | 19.6 |
| | Aug | 213 | 17.7 | 133.3 | 16.6 | 147.6 | 17.5 | 175.1 | 19.3 |
| | Sep | 212 | 17.9 | 129.1 | 16.1 | 156.2 | 17.7 | 173 | 19.2 |
| | Oct | 212 | 18 | 127.8 | 16.5 | 172 | 18.3 | 170.2 | 19.4 |
| | Nov | 211 | 18.1 | 130 | 16.5 | 173.1 | 17.7 | 167.6 | 19.3 |
| | Dec | 208 | 18.8 | 128.9 | 17.3 | 179.3 | 18.3 | 165.8 | 19.4 |
| 2015 | Jan | 205 | 18.4 | 127.1 | 16.8 | 177.1 | 19.7 | 161.1 | 20 |
| | Feb | 204 | 18.6 | 126.5 | 17 | 180.3 | 18.5 | 165.7 | 20.5 |
| | Mar | 200 | 18.3 | 127.3 | 16.8 | 182.1 | 17.1 | 162.7 | 20.6 |
| | Apr | 202 | 18.2 | 124.9 | 18.1 | 184.5 | 18.1 | 163.1 | 20.6 |
| | May | 202 | 18.1 | 126.7 | 16.5 | 182.1 | 17.9 | 160.3 | 20.1 |
| | June | 205 | 17.7 | 130 | 15.8 | 177.7 | 17.3 | 163.5 | 19.5 |
| | July | 207 | 17.3 | 129.7 | 15.4 | 172.4 | 17 | 167.6 | 19.3 |
| | Aug | 207 | 17.6 | 131.9 | 16 | 161.5 | 16.8 | 170 | 19.2 |
| | Sep | 206 | 18 | 130.3 | 16.2 | 166.8 | 17.3 | 169.5 | 19.7 |
| | Oct | 206 | 18.9 | 134.5 | 16.7 | 175 | 17.7 | 165.8 | 20.2 |
| | Nov | 208 | 18 | 129.9 | 16.4 | 177 | 18 | 166 | 19.7 |
| | Dec | 207 | 19.3 | 127.8 | 16.5 | 178.6 | 17.6 | 163.2 | 20.2 |
| 2016 | Feb | 204 | 18.7 | 127 | 16.9 | 179.5 | 18.1 | 165.5 | 20.3 |
| | Mar | 200 | 18.5 | 127 | 16.3 | 180 | 17.7 | 163 | 20.1 |
| | Apr | 202 | 18.4 | 127 | 16.5 | 173 | 17.7 | 160 | 20.7 |
| | May | 202 | 18 | 127 | 16.2 | 170 | 17.5 | 159 | 20.2 |
| | June | 205 | 17.9 | 130 | 16.2 | 165 | 17.4 | 164 | 19.7 |
| | July | 207 | 17.7 | 130 | 16 | 165 | 17 | 166 | 19.4 |
| | Aug | 207 | 18.6 | 129 | 16.1 | 160 | 17.3 | 168 | 19.8 |
| | Sep | 206 | 17.6 | 125.8 | 16.1 | 165.1 | 17.1 | 166.5 | 18.9 |
| | Oct | 206 | 19 | 125.1 | 16.6 | 168 | 17.6 | 166 | 20.3 |
| | Nov | 206 | 18.3 | 126 | 16.8 | 170 | 17.9 | 161 | 21.3 |
| | Dec | 216 | 18.3 | 120 | 16.4 | 170.7 | 17.8 | 165.7 | 19.6 |

The temperature and springs EC values graph was plotted to detect if there is a correlation between the two variables. Newlands spring has the lowest EC values and the lowest temperatures. The other three springs' show no correlation between EC and Temperature. Albion spring has the highest EC but does not have the highest temperature; De Waal spring has the warmest water (Figure 26). There is no correlation between the EC values of the springs and temperature.

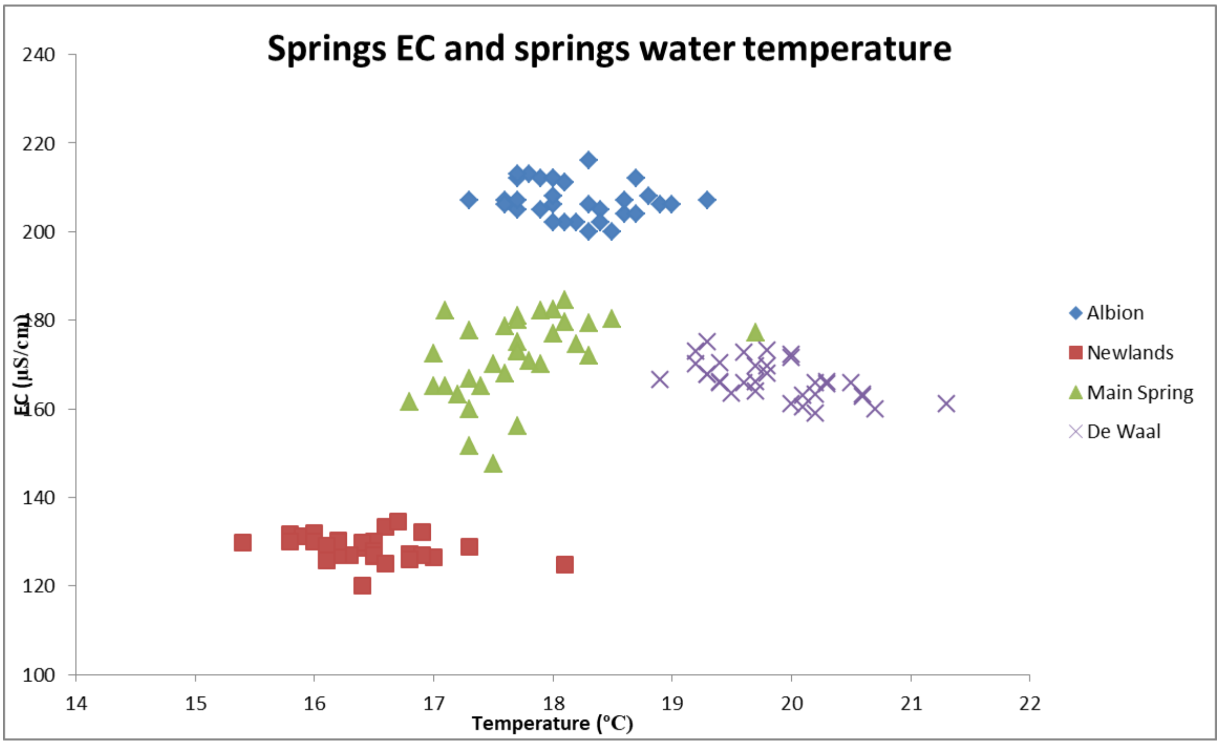


**Figure 26. Springs water temperature and EC values.**

The EC values of the spring waters are expected to be low because they are freshwater springs see the average EC values in (Table 10). The recorded EC values for the springs are relatively constant, the average EC values for each of the spring is; Albion spring 207 µS/cm, Newlands spring 128 µS/cm, Main spring 171 µS/cm and De Waal 166 µS/cm. Albion spring has the highest EC values and Newlands the lowest values. The high EC values of Albion spring show that it has the highest concentration of TDS. The springs EC values and altitude (Table 12) shows that, Albion spring has got the highest EC and situated at an altitude 20 mamsl (lowest).

**Table 12. Springs altitudes and average EC values.**

| Spring | Altitude (mamsl) | Average EC (µS/cm) |
|---|---|---|
| Albion | 20 | 207 |
| De Waal | 60 | 166 |
| Main Spring | 115 | 171 |
| Newlands | 40 | 128 |

In order to investigate the source of EC in the groundwater, EC values were plotted against the isotope composition of the springs. Firstly the EC values at each spring did not appear to have a seasonality effect, the EC readings remained constant throughout the year. Secondly, there was no correlation between the isotope data and EC, see (Figure 27). The Albion spring has the highest EC values and this is not correlated to the isotope data of the spring. There is very little correlation between the $\delta^{18}O$ value and EC values for any of the springs' samples; this is the same with $\delta D$ and EC.

In general groundwater in the table mountain group Aquifer is among the lowest in term of EC. Rosewarne (2002) wrote that the EC is normally in the range 50 to 100 mS/m (500 to 1000 µS/cm) for groundwater in coastal mountain catchment, the study was between Cape Town and Port Elizabeth, the EC values from the Table Mountain springs is lower than this. In some cases the EC might be above the expected range and this could be the results of seawater intrusion, for example Weaver (1998) investigated sources of Salinity which resulted in high EC values in the Struisbaai groundwater and concluded that salinity in groundwater from old wellfield was probably due to a degree of seawater intrusion. In Hermanus as well, von Scherenberg & Seyler (2012) wrote that due to the complex fault system in the fractured rock of the Peninsula Aquifer, this has resulted in the saline intrusion in the groundwater. Harris et al. (2000) showed that the most of the Cape Flats aquifer samples had EC in the range 500-1000 µS/cm, but isotopically they had no sea water.

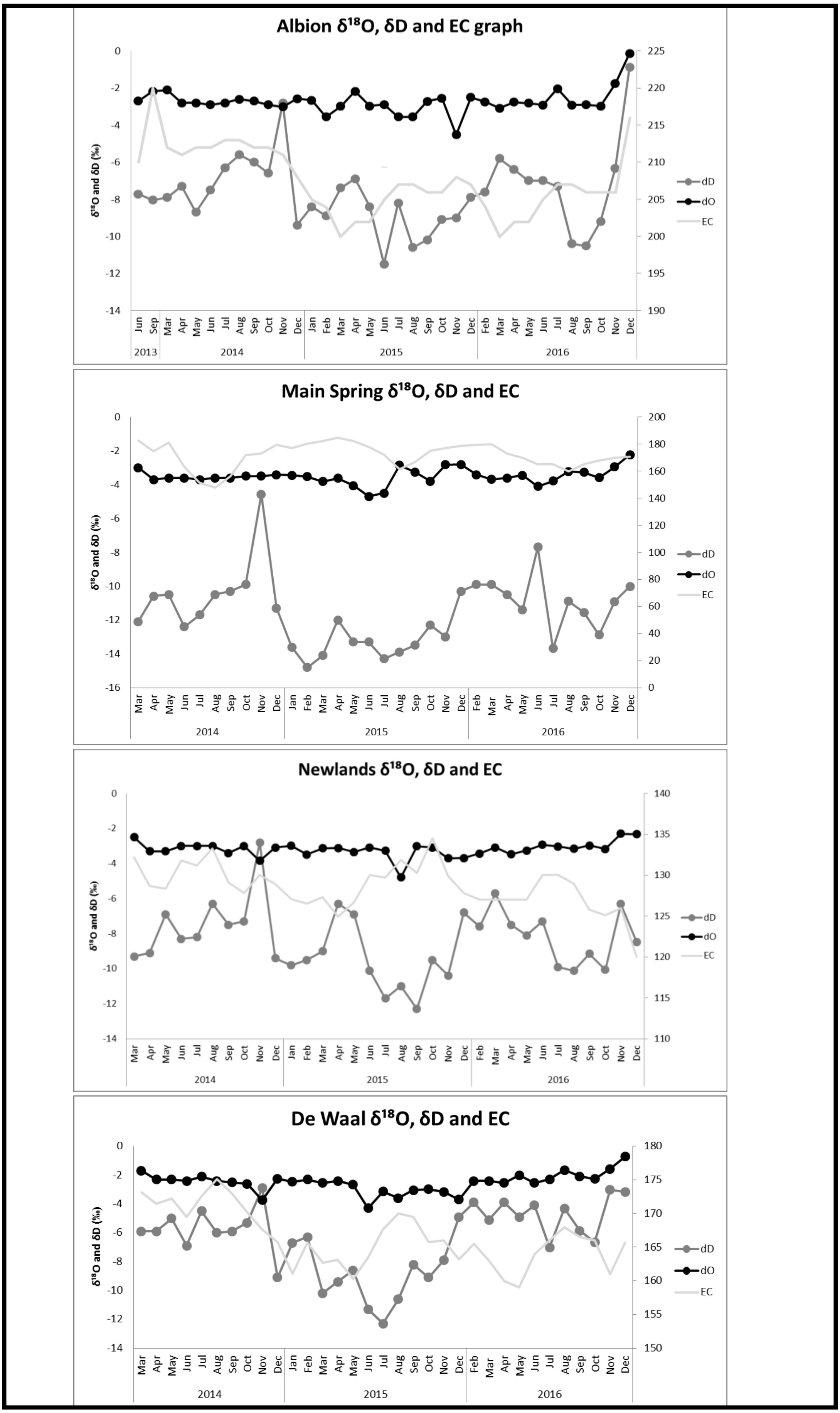


**Figure 27. Plot of isotope data and EC values for each spring.**

### 4.4.2 Isotopic Compositions of springs

All the springs' δD vs $\delta^{18}$O data was plotted on one graph in (Figure 28), and (Figure 29) is showing the average δD and $\delta^{18}$O values of each spring for each year from 2013 to 2016. (Figure 30) displays each spring individual plot. The springs appear to be well grouped, and plot in isotopically distinct fields. The Main spring (Figure 30c) has the lower δD and $\delta^{18}$O values, with Newlands and Albion spring having an intermediate δD and $\delta^{18}$O composition, and De Waal spring having highest δD and $\delta^{18}$O values. De Waal spring scatter is more noticeable than the other springs see. The springs have got average mean δD and $\delta^{18}$O values of -7.7 and -2.74‰ for Albion spring, -6.48 and -2.46‰ for De Waal spring, -11.52 and -3.48‰ for Main spring and -8.49 and -3.14‰for Newlands spring.

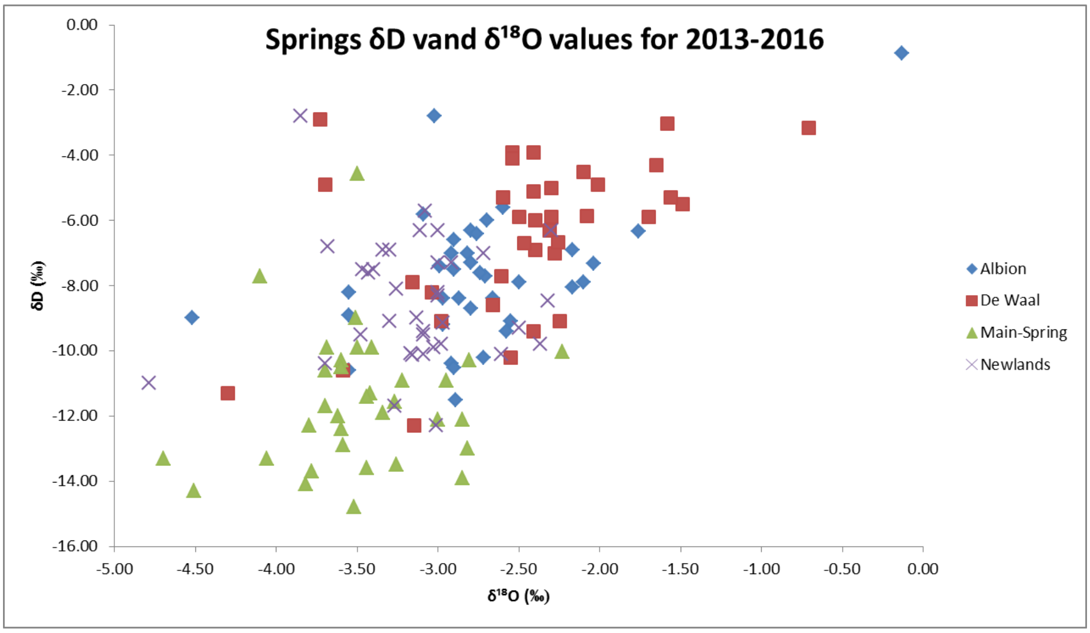


**Figure 28. Plot of springs 2013 to 2016 δD and $\delta^{18}$O values for all four springs.**

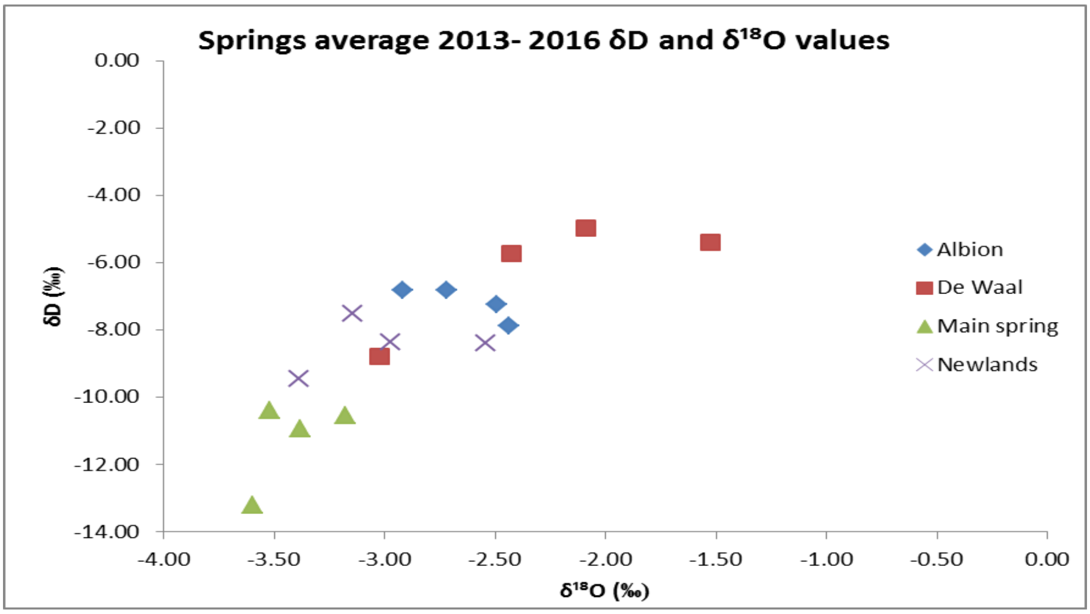
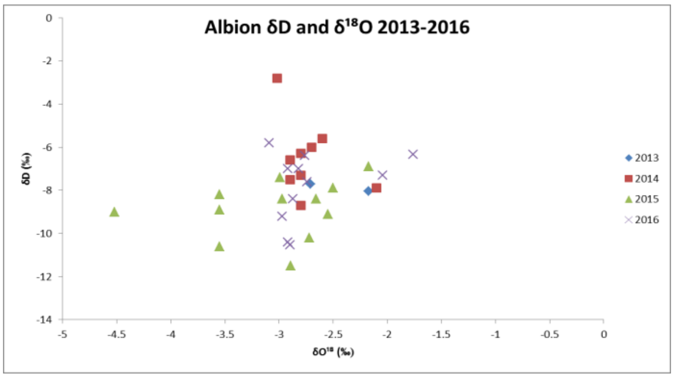
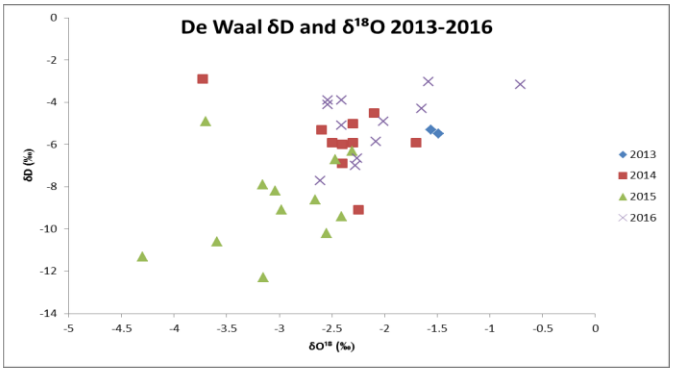


**Figure 29. Average means δD and $\delta^{18}$O values of the springs for each year from 2013 to 2016.**

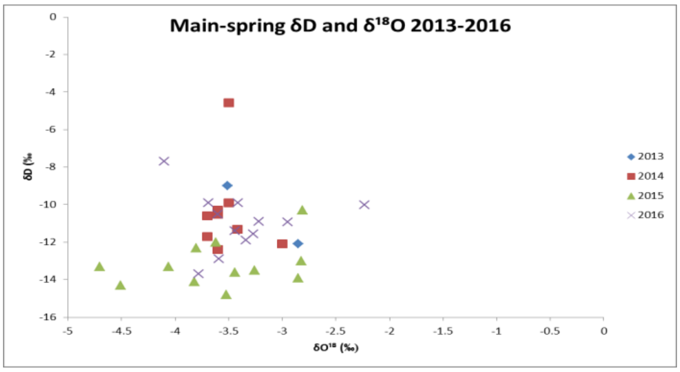
29a. Albion spring



29b. De Waal spring



29c. Main-spring



29d. Newlands spring

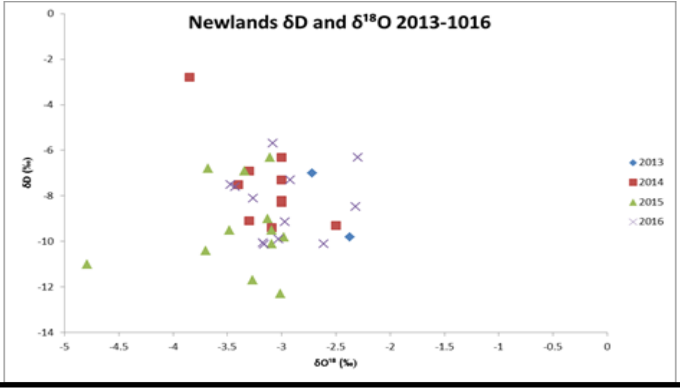


**Figure 30. (a) Albion spring, (b) De Waal spring, (c) Main spring and (d) Newlands spring individual δD and $\delta^{18}$O plots.**

The average means $\delta^{18}O$ of springs investigated in this study and the springs sampled in Harris et al. (2010) were plotted against the springs' altitudes to see if there was a correlation between the two variables (Figure 31). This was to see if there is an altitude effect on the springs. The Cable Way spring is located at the highest altitude and has got the lowest $\delta^{18}O$ values. The Albion spring is situated at the lowest altitude at 20 mamsl, but does not have the highest $\delta^{18}O$ values, instead De Waal spring had higher $\delta D$ and $\delta^{18}O$ values, but situated at an altitude of 60 mamsl. The graph shows a trend of high elevation, low $\delta^{18}O$ values for most of the springs, with the exception of Albion spring. Therefore it appears as if the isotopic composition of the springs is influenced by the altitude effect. In Harris et al. (1999) the Table Mountain springs results showed slight evidence of altitude effect.

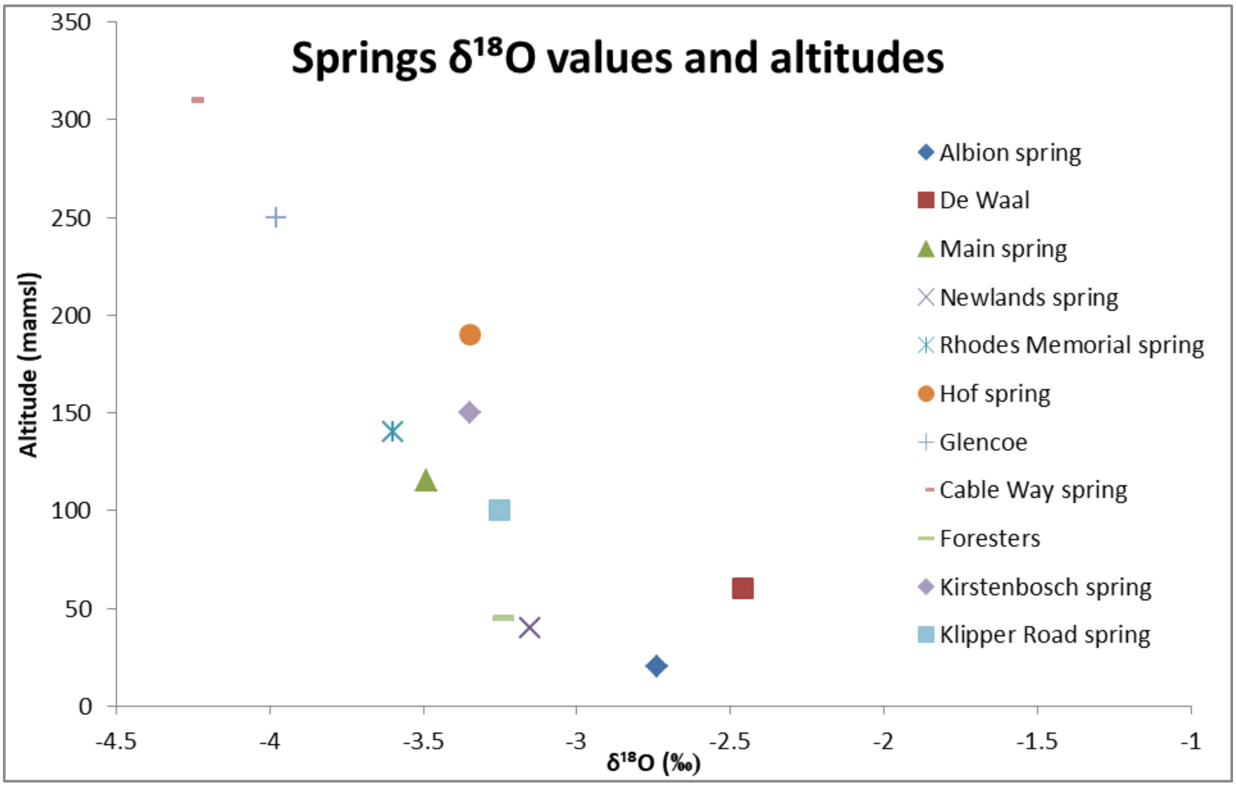
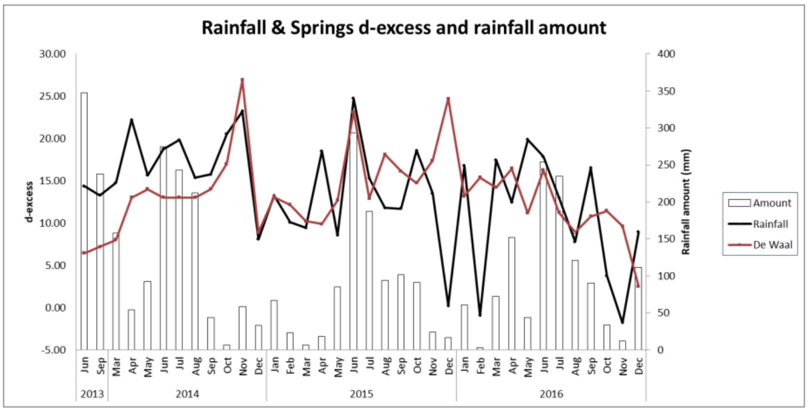


**Figure 31. Average mean $\delta^{18}O$ data of the springs studied in this work and other springs' studied from Harries et al. (2010) vs altitude.**

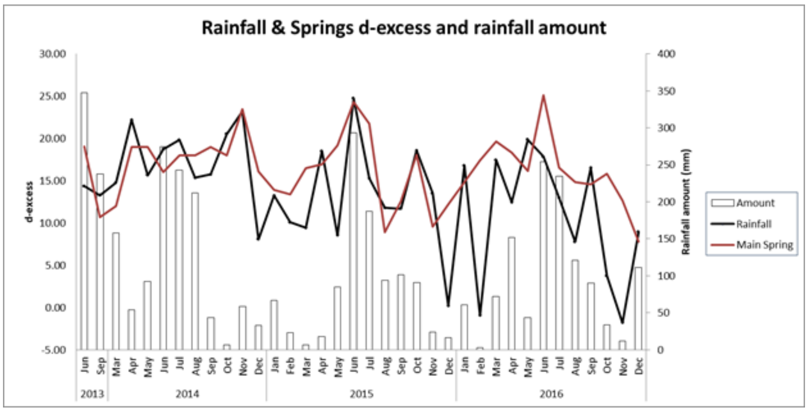
The d-excess of the rainfall range between -11.56 to 33.12, and for the springs; De Waal spring 2.51 to 26.91, Main spring 7.82 to 25.1, Newlands spring 9.16 to 27.97, and Albion spring 0.17 to 27.16, see (

Table **13**).The average mean d-excess for the rainfall is 11.19 and for each of the springs is; De Waal spring 13.34, Main spring 16.37, Newlands spring 16.63 and Albion spring 14.22. De Waal spring has got the highest $\delta D$ and $\delta^{18}O$ values with the lowest average d-excess values. Low d-excess values are usually associated with low $\delta D$ and $\delta^{18}O$ values or highly depleted samples. (Figure 32) shows a general trend between the springs and the rainfall d-excess, the d-excess for the rainfall and springs decreases and increases at the same time. The summer months (low rainfall) have relatively lower d-excess values than the winter months (higher rainfall). There is positive relationship between the rainfall d-excess, springs d-excess and the rainfall amount, as the amount of rainfall increases the d-excess values of both the rainfall and springs increase.

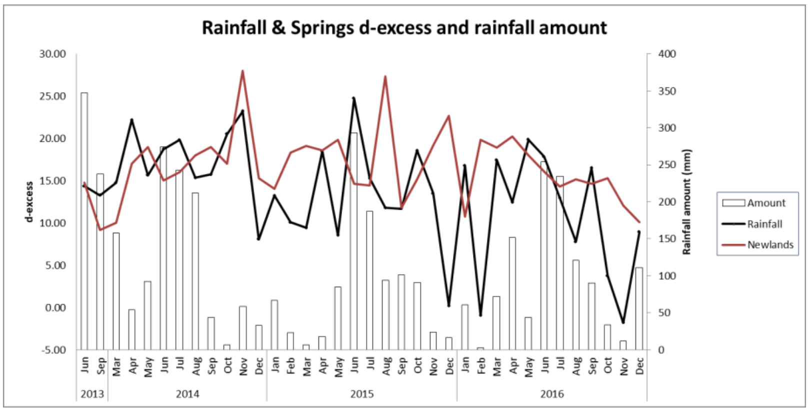
a) De Waal spring



b) Main spring



c) Newlands spring



d) Albion spring

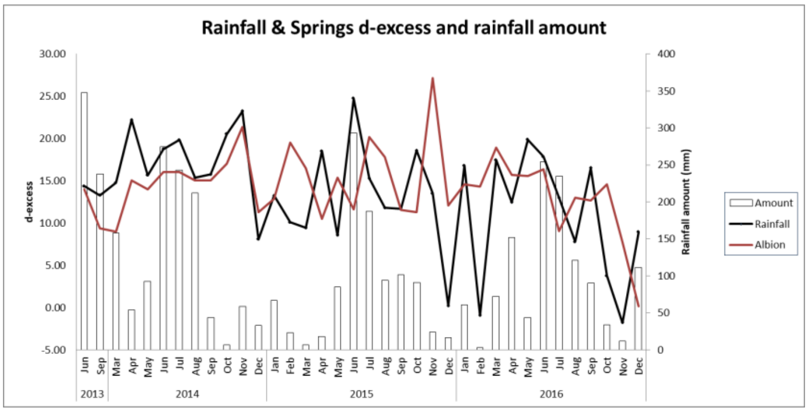


**Figure 32. The 2013- 2016 d-excess values of UCT rainfall and the four springs, and rainfall amount.**

**Table 13. The d-excess values of the Albion spring, Newlands spring, De Waal spring, and Main spring.**

| | | d-excess | | | | |
|---|---|---|---|---|---|---|
| Year | Month | Rainfall | De Waal | Main spring | Newlands | Albion |
| 2013 | Jun | 14.36 | 6.42 | 19.08 | 14.76 | 13.96 |
| | Sep | 13.28 | 7.18 | 10.70 | 9.16 | 9.36 |
| 2014 | Mar | 14.74 | 8.00 | 12.00 | 10.00 | 9.00 |
| | Apr | 22.20 | 13.00 | 19.00 | 17.00 | 15.00 |
| | May | 15.64 | 14.00 | 19.00 | 19.00 | 14.00 |
| | Jun | 18.75 | 13.00 | 16.00 | 15.00 | 16.00 |
| | Jul | 19.81 | 13.00 | 18.00 | 16.00 | 16.00 |
| | Aug | 15.33 | 13.00 | 18.00 | 18.00 | 15.00 |
| | Sep | 15.75 | 14.00 | 19.00 | 19.00 | 15.00 |
| | Oct | 20.52 | 17.00 | 18.00 | 17.00 | 17.00 |
| | Nov | 23.21 | 26.91 | 23.43 | 27.97 | 21.36 |
| | Dec | 8.08 | 8.90 | 16.06 | 15.32 | 11.26 |
| 2015 | Jan | 13.22 | 13.06 | 13.92 | 14.04 | 12.88 |
| | Feb | 10.06 | 12.14 | 13.37 | 18.32 | 19.50 |
| | Mar | 9.41 | 10.21 | 16.46 | 19.09 | 16.51 |
| | Apr | 18.50 | 9.88 | 16.96 | 18.58 | 10.46 |
| | May | 8.53 | 12.68 | 19.18 | 19.82 | 15.36 |
| | Jun | 24.74 | 23.10 | 24.30 | 14.62 | 11.62 |
| | Jul | 15.28 | 12.90 | 21.78 | 14.46 | 20.20 |
| | Aug | 11.79 | 18.12 | 8.90 | 27.32 | 17.80 |
| | Sep | 11.70 | 16.12 | 12.58 | 11.78 | 11.56 |
| | Oct | 18.57 | 14.71 | 18.07 | 15.18 | 11.30 |
| | Nov | 13.50 | 17.38 | 9.56 | 19.20 | 27.16 |
| | Dec | 0.20 | 24.70 | 12.18 | 22.64 | 12.10 |
| 2016 | Jan | 16.8 | 13.18 | 14.82 | 10.78 | 14.56 |
| | Feb | -0.94 | 15.38 | 17.38 | 19.84 | 14.32 |
| | Mar | 17.44 | 14.18 | 19.62 | 18.94 | 18.92 |
| | Apr | 12.44 | 16.42 | 18.3 | 20.26 | 15.68 |
| | May | 19.86 | 11.18 | 16.12 | 17.98 | 15.56 |
| | Jun | 17.84 | 16.22 | 25.1 | 16.06 | 16.36 |
| | Jul | 12.99 | 11.23 | 16.55 | 14.33 | 9.01 |
| | Aug | 7.76 | 8.89 | 14.86 | 15.16 | 12.96 |
| | Sep | 16.5 | 10.77 | 14.6 | 14.62 | 12.68 |
| | Oct | 3.76 | 11.42 | 15.84 | 15.29 | 14.56 |
| | Nov | -1.8 | 9.62 | 12.68 | 12.09 | 7.75 |
| | Dec | 8.94 | 2.51 | 7.82 | 10.09 | 0.17 |

### 4.4.3 Summary

Rainfall data from 1995/6 to 2016/12 was used to calculate the LMWL and the local meteoric water line equation is $\delta D = 6.03*\delta^{18}O + 7.07$. The rainfall isotope data was also analysed by calculating means and weighted means, d-excess values for these means. The dataset showed the amount effect, winter months the δD and $\delta^{18}O$ values are lower than summer months. As the temperatures decreased during the winter months, δD and $\delta^{18}O$ values become lower; there is an obvious seasonality effect on the data. The d-excess varies between summer and winter; the d-excess values seem to be higher during the winter months and lower during the summer months. There is a positive relationship between the rainfall amount and d-excess (Figure 32) with a correlation coefficient of ($r = 0.34$) and a negative relationship between temperature and d-excess (Figure 24).

The stable isotope data for each of the four springs have its own distinct signature. Main spring has the lowest δD and $\delta^{18}O$ values, while De Waal has the highest δD and $\delta^{18}O$ values. Overall the springs' isotope data is less scatted than the rainfall isotope data, springs data is more tightly clustered than rainfall. The springs' isotope data plot mostly above the LMWL line. The rainfall d-excess and the spring d-excess have a strong positive relationship (Figure 32). Albion spring has the highest EC values and Newlands the lowest EC values. There is no correlation between the EC values of the springs' with temperature, altitude, and isotopic composition of the springs. EC values distinct for each spring throughout time of sampling, there was no overlap between the springs.

# Chapter 5 Discussion

## 5.1 Introduction

This chapter is made up from three parts. The first part contains and discusses results on the isotope data for the rainfall and the springs (groundwater). The second part is an attempt to give or estimate a recharge rate of the springs; and the last part discusses the analysis of the hydrochemical properties of the springs' water. Factors such as meteorological conditions (evaporation), altitude, temperature, and the amount of rainfall will explain the variation of the stable isotopes. Isotope data of rainfall is presented and compared with the isotopic compositions of the springs to answer the main question of this project.

## 5.2 Isotopic signatures

### 5.2.1 Isotopic signatures in the rainfall

Amount effect

Dangaard (1964) wrote that there is a correlation between δD and $\delta^{18}O$ and rainfall amount. What he wrote is, as the amount of rainfall increases, the δD and $\delta^{18}O$ values decrease, and the opposite is true. Many authors have since described the same findings in different regions around the world. Graphically the plot of δD and $\delta^{18}O$ vs the monthly amount shows good correspondence, on average the winters months have rainfall with lower δD and $\delta^{18}O$ values than the summer months. The monthly δD and $\delta^{18}O$ values are high in the summer months, (Figure 21). Correlation coefficients values were calculated for the δD, $\delta^{18}O$ values, and the monthly rainfall amount and the correlation coefficient between δD and the rainfall amount is ($r = -0.60$) and the correlation coefficient between $\delta^{18}O$ is ($r = -0.61$). The correlation coefficient confirms what is observed on the graph or the visual impressions given by the graph. From both correlation coefficient values and the graph, there is a relative strong negative correlation between rainfall amount and isotopic composition. The amount affect is generally noticeable and there is a good correlation between δD and $\delta^{18}O$ values and rainfall amount. The amount effect is one of the factors that influence the isotope composition of the rainfall.

Temperature effect

Figure 21 also shows the relationship between the average monthly temperatures and isotope composition of the rainfall. When the temperature increases, the δD and $\delta^{18}O$ values increase as well. The correlation coefficient between δD and $\delta^{18}O$ and the temperature show a positive strong correlation. The correlation coefficient between δD and temperature is ($r = 0.87$) and between $\delta^{18}O$ and temperature is ($r = 0.62$). The graphs and the correlation coefficients values confirm a strong positive correlation between the isotopic composition of the rainfall and temperature.

Seasonal effect

Cape Town receives its rainfall season during the winter season and has dry summers. There is an inverse relationship between the amount of rainfall and the temperature when the temperature increases during summer months the amount of rainfall decrease (Figure 33). The temperature and the rainfall amount are two factors that correlate with the isotope composition of rainwater. There is a strong relationship between isotope composition of rainfall and temperature. There is a positive correlation between the temperature and isotope composition and a negative correlation with the rainfall amount. The data of the four years plotted shows the same pattern, for example in 2016 during the summer months (October- March) the average mean δD and $\delta^{18}O$ values was -1.51 and -1.11 ‰ with an monthly average rainfall of 48.8 mm and for the winter month (April-September) with the average mean δD and $\delta^{18}O$ values-11.0 and -3.20 ‰ with an monthly average rainfall of 149.2 mm. This shows a strong seasonal effect, which is driven by the temperature and the amount of rainfall. When you look at the summer and winter months, there is a clear seasonal difference in the isotope composition. If the springs' isotope data reflect the same seasonal effect as the rainfall, this will show that the rainfall is the source of the spring recharge water.

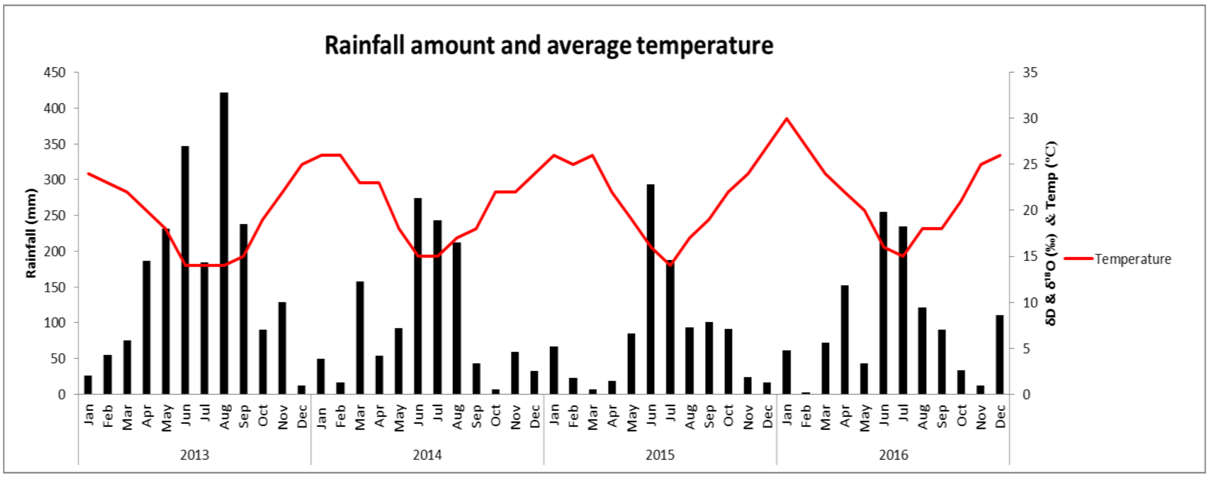


**Figure 33**. **Plot of rainfall amount and average monthly temperatures.**

### 5.2.2 Meteoric water lines

Source area

The rainfall in the Western Cape Province is dominated by winter frontal rain, while central and northern parts of the country experience summer rainfall brought over by South Indian High-Pressure cell. As described above the local meteoric water line equation based on 21 years monthly rainfall data is $\delta D = 6.03*\delta^{18}O + 7.07$. Harris et al. (2010) Calculated the line of best fit for rainfall data from 1995 to 2008 to have the equation of $\delta D = 6.41*\delta^{18}O + 8.66$. The data set presented in this thesis gives a local meteoric water line that is closely similar previously calculated equation. The local meteoric water line has a less steep gradient than the global meteoric water line, (Figure 23).

### 5.2.3 Isotopic composition of the spring water

Each spring has got its own distinct signature, with Main spring having lowest δD and $\delta^{18}O$ values, Albion and Newlands spring with an intermediate isotopic composition and De Waal spring having the highest δD and $\delta^{18}O$ values. The reason could be each spring is recharged by water flowing in its own underground flow path, and mixing of meteoric water takes place during recharge, averaging out the composition of discharge. The other reason could be the potential recharge zones of each spring are located at different altitudes. The springs' isotope data and the rainfall isotope data were plotted together (Figure 34). Despite the fact that each spring has got its own distinct isotope composition signature, the springs isotopic composition changes are subtle compared to the rainfall. The difference between the two datasets is the lack of scattering is noticeable with the springs data contrast to the rainfall data, but springs' data fit into the rainfall data. The rainfall is the source of recharge for the springs.

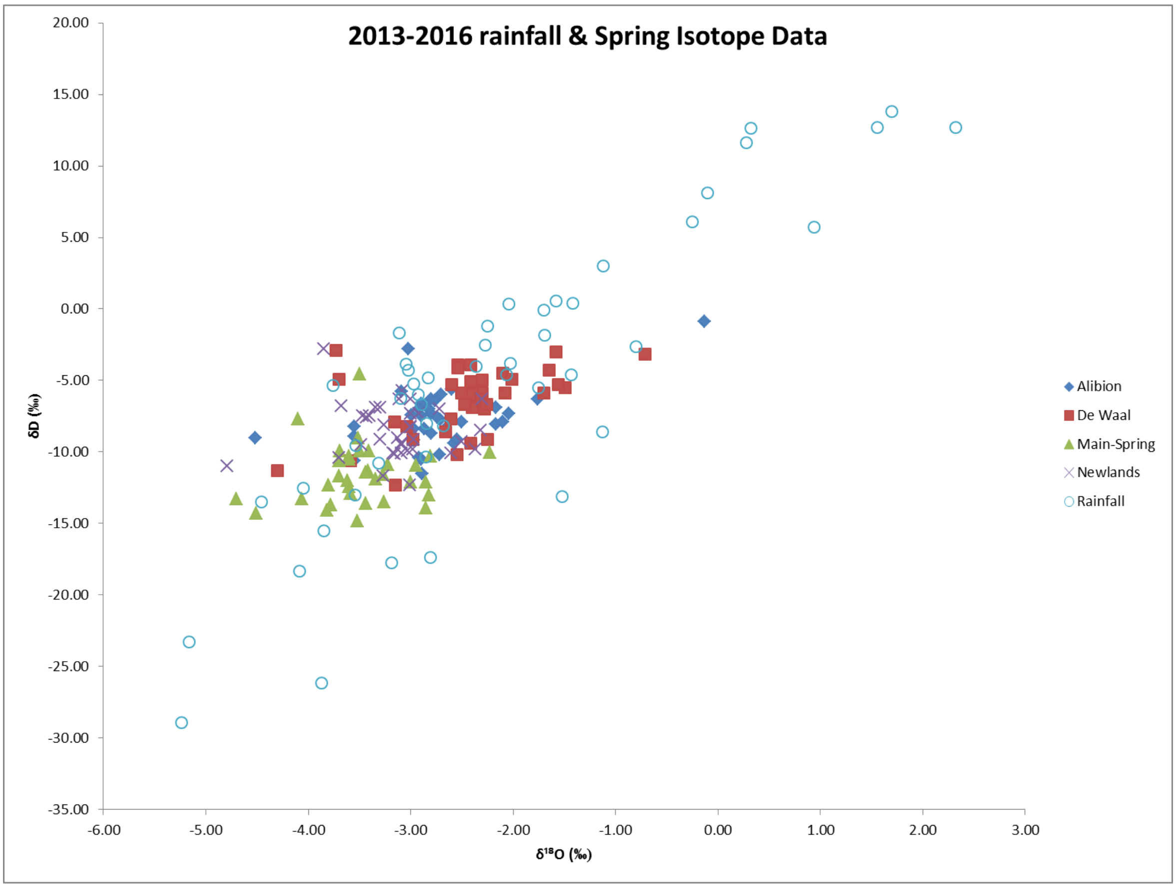


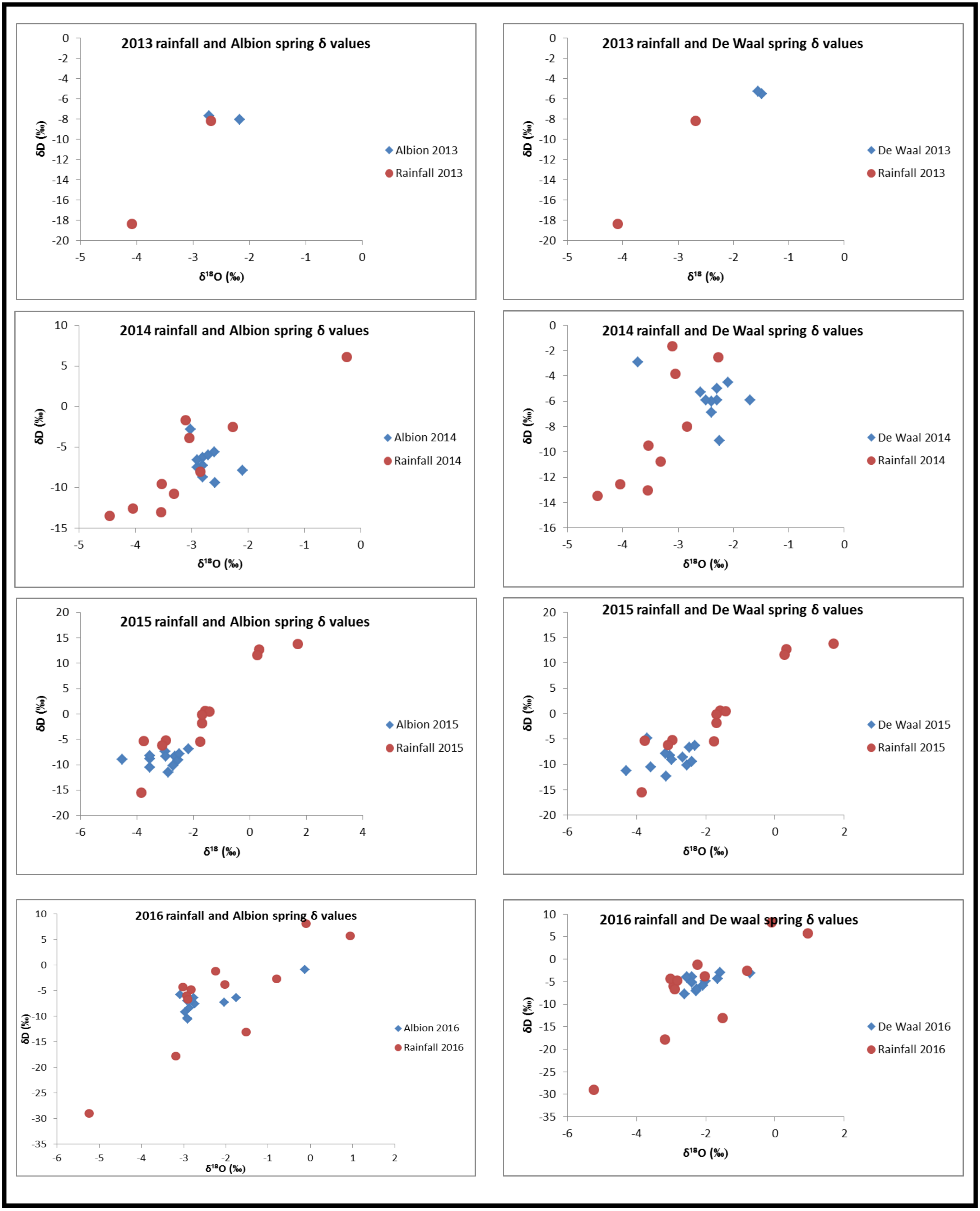
**Figure 34. Plot of δD and δ$^{18}$O of the springs and UCT rainfall data, rainfall data is more scatted.**

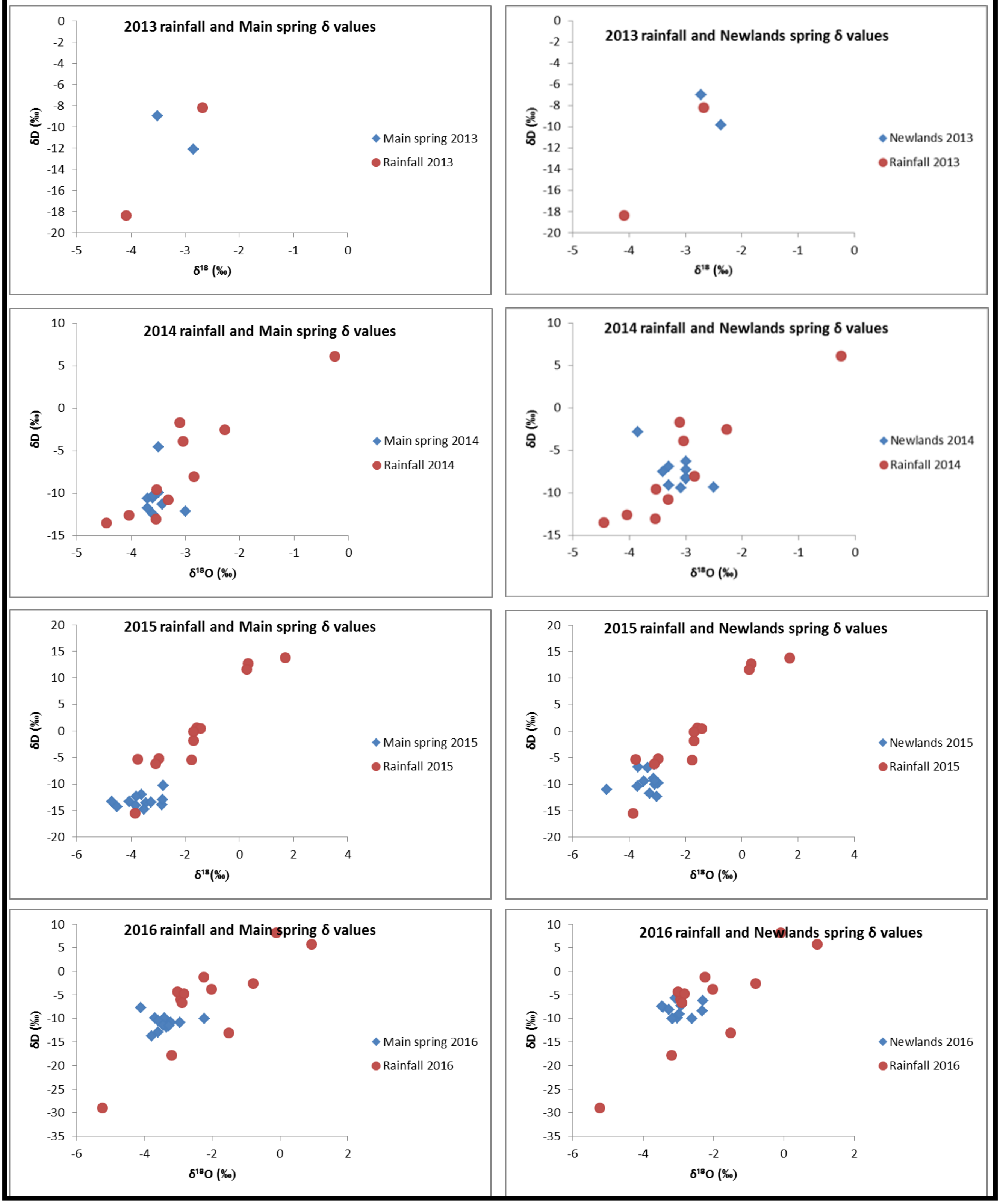
### 5.2.4 Isotope composition of the springs and rainfall time series

The springs δD and δ$^{18}$O values are negative, as winter rainfall has lower δD and δ$^{18}$O values than summer rainfall, therefore the springs are recharged by the winter rainfall. Each spring and rainfall δD and δ$^{18}$O values for each year from 2013 to 2016 are plotted in (Figure 35). The δD and δ$^{18}$O values for the springs indicate that there is no overlap for 2013 to 2014, there is a significant shift occurs of isotope values from 2013 to 2014. No samples from 2013 fall within the range of 2014 samples. One explanation could be that in 2013 the springs were sampled only twice in June and September, and the springs were sampled more regularity from 2014. The rainfall samples between 2013 and 2014 also show a significant shift, 2013 is by far the wettest year in the years investigated in this study. From 2014 when the springs were sampled on a monthly base, there seem to be an overlapping pattern emerging. The change in the isotopic composition of the rainfall from 2013 to 2016 is reflected in the springs from 2014 to 2016. This is evident in all the springs, but if we take Albion springs (Figure 35.a) as an example, the change in the isotopic composition of the rainfall from 2014 appears to be reflected in the 2015 spring water, and is the same for the subsequent years 2015 rainfall is reflected in the 2016 spring water. The δD and δ$^{18}$O values of the 2015 Albion spring water is similar to the δD and δ$^{18}$O values for 2014, therefore one can assume that the spring is recharged by the 2014 rainfall, concluding that the δD and δ$^{18}$O values for the rainfall are a good approximation to the δD and δ$^{18}$O values of the spring water, which represent recharge. The similarities in the isotopic composition of the springs' δD and δ$^{18}$O values from year to year can be interpreted as rainfall water mixing with water in the aquifer. The isotopic composition of the 2016 rainfall is distinctly different from the 2015 rainfall and the change is reflected in the spring, with 2016 rainfall similar to the springs δD and δ$^{18}$O values, therefore one can conclude that the 2016 rainfall is a part of the recharge feeding the 2016 spring water.

(a) Albion spring

(b) De Waal spring





(c) Main spring

(d) Newlands spring

**Figure 35. The δD and $\delta^{18}$O values plot for the four springs and rainfall for each year from 2013-2016. (a) Albion spring, (b) De Waal spring, (c) Main spring and (d) Newlands spring.**

When all the isotopic data of the springs and rainfall are plotted on the same graph, the springs plot close to the local meteoric water line, mostly just above and some just below. The springs' isotope composition is not very different from the meteoric water. The rainfall average means δD and δ$^{18}$O is -7.85 and -2.47 ‰ and for Albion spring -7.68 and -2.74 ‰, De Waal spring -6.45 and -2.46 ‰, Main spring -11.51 and -3.49 ‰ and Newlands spring -8.44 and -3.15 ‰. The δD and δ$^{18}$O values of springs' samples collected lie closely around the local meteoric water line, confirming that the groundwater is recharged by the rainfall, see (Figure 23).

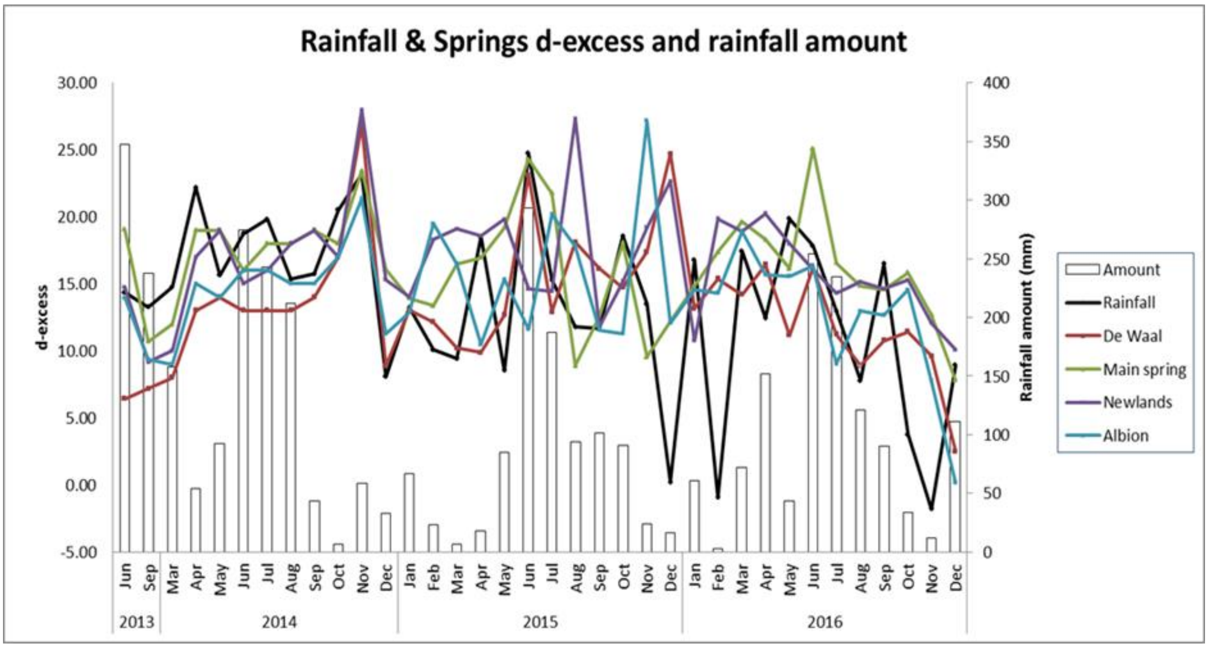


**Figure 36. The d-excess values for UCT rainfall and the four springs**

Figure 36 show the d-excess for the rainfall samples with a range of -11.56 to 33.12 with an average of 11.19. Seasonal variation of d-excess is obvious, for summer the low d-excess implies that precipitation was low; the winter rainfall shows higher d-excess values suggesting that the winter receives more rainfall. This is consistent with the high δD and δ$^{18}$O values in summer and the low winter isotopic composition. There is a positive correlation coefficient between the d-excess and rainfall amount ($r = 0.34$).These values shows that the rainfall amount slightly influence the values of d-excess. The d-excess is probably related to other conditions for example, some evaporation during descent in rainfall. From the rainfall d-excess values, the summer rainfall is more evaporated than the winter rainfall. The change in the springs' d-excess values clearly mimics that of the rainfall, whereas δD and δ$^{18}$O values on their own tend to be ambiguous, d-excess values can support the findings of the δD and δ$^{18}$O values, (Figure 32) show plot of each individual spring. The similar pattern changes of the d-excess values and δD and δ$^{18}$O of the rainfall is reflected in the spring water at a short period, suggesting that recharge is occurring rather rapidly and from the d-excess values, the recovery seem to occur from month to month (within month) for some springs and more months for others (

Table **13**). This is inferred as with every monthly change in the rainfall d-excess values, the springs d-excess values also changes.

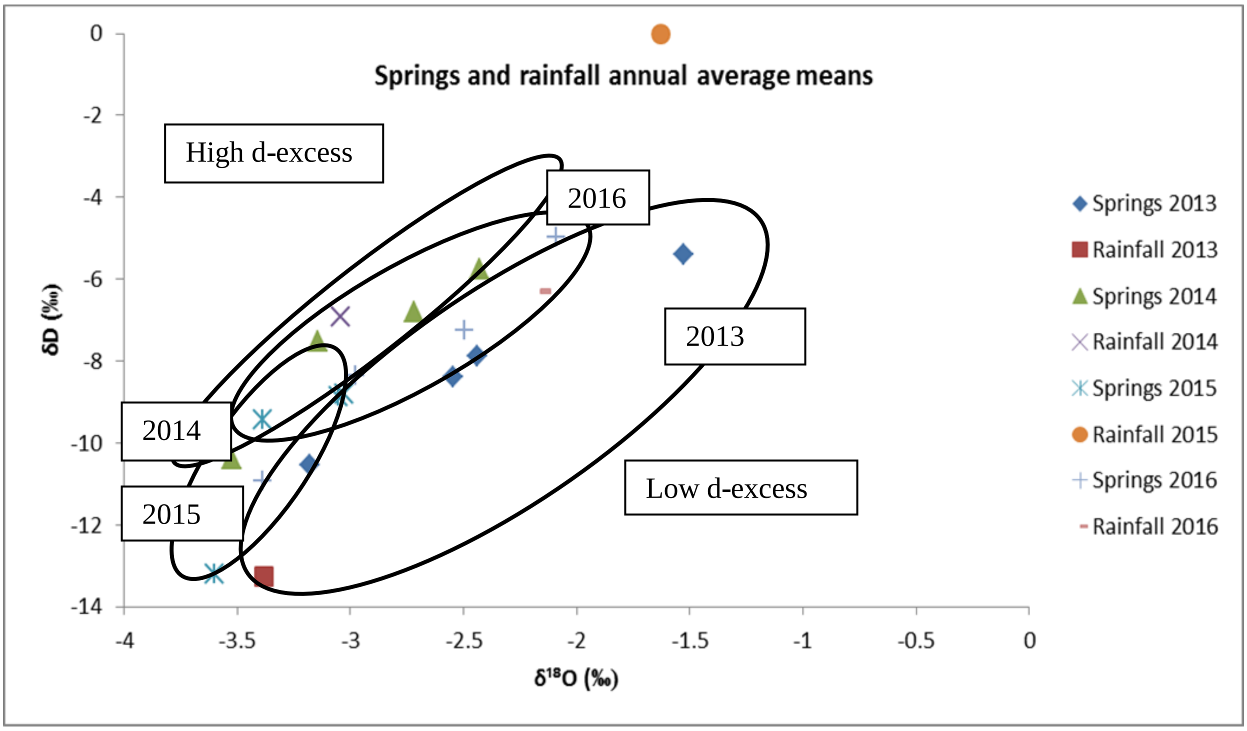


**Figure 37**. **Springs and rainfall annual average means δD and $\delta^{18}$O plotted according to each year.**

The d-excess of the spring follow the same pattern as that of the rainfall. This is further confirmation that the springs are recharged by the rainfall. The seasonal variability is mostly influenced by temperature and rainfall amount. All this data can give an estimate of the recharge rates. Using d-excess to estimate recharge rates is more reliable than δD and $\delta^{18}$O because d-excess changes can clearly be recognised in both rain and spring water. (Figure 37) shows the average annual mean δ values of the rainfall and the springs. From 2014 to 2016 springs' data and rainfall dataset, one can conclude that recharge is occurring rapidly with the recovery taking one month as seen from the d-excess values. Previously Harris et al. (2010) noted from the 1996-2008 rainfall dataset and the springs, that recharge was very rapid with at least 50% recharge possibly being effective within three years. The recovery rate shows that the springs are recharged by the local rainfall; the aquifer is situated on the lower slopes of the mountain. (Figure 32) shows the individual springs' d-excess and the rainfall d-excess, from the diagrams De Waal spring mimics the rainfall d-excess very closely, the changes are almost at the same time, this means that the De Waal spring is recharged the fastest, recovery occurs from month to month. Newlands d-excess does not change at the same time at the rainfall's d-excess, Newlands is the slowest spring to recover, with recharge occurring at least within three months. Main spring and Albion spring fall in between the fastest and slowest recovery spring. The springs are recharged at different rates but with the general average of recharge rate of one to three months recovery. The springs are recharged by rainfall and the winter rainfall seems to be the main source of the spring recharge. An explanation for the rapid recharged is explained by the combination of rainfall that recharges the Peninsula Aquifer and the shallow Scree Aquifer for the springs. Recharge from the Scree Aquifer could be a lot more rapid than the Peninsula Aquifer, but the Peninsula Aquifer support the Scree Aquifer to maintain recharge occurring on a yearly basis (Figure 8).

## 5.3 Recharge of the aquifer

The springs and the rainfall have the same shift annual pattern, with a slight difference in the isotope composition, this shifts could suggest that the springs discharge groundwater that has been recharged in the same year. Diamond (2015) wrote that if the Table Mountain springs discharged recharged water from the same year, the spring would only flow during the rainfall season (winter months) and stop flowing during the summer months. The four springs in this study are perennial springs and flow all year long, this support the conclusion that the springs are recharged by both the Peninsula Aquifer and the Scree Aquifer. The two aquifers are able to maintain flow pass the rainy season. This is proven by the fact that the springs recharge water isotope composition is similar to the rainfall isotope composition of the same year.

### 5.31 Recharge Zone

Oxygen and hydrogen stable isotopes can be described as isotope tracers because they can be monitored to determine distribution and recharge rate of the recharge water (rainfall). This means that recharge water isotopic signature should be evident in the outlet water samples. The springs emerge from large scree deposits that cover the north-east slopes of Table Mountain. But because of the similar isotope composition with the rainfall, this in turn means long distance groundwater flow is probably not occurring. As the trend observed is based on the isotopic values of springs, and the springs are recharge by the rainfall in the recharge area, this means the positions of springs' are close to the position of the recharge zone. Recharge zone is an area of land where water collects when it rains and stored in the aquifer in the area. The average mean annual precipitation is 1400 mm in the recharge area. The mean average isotope composition for UCT rainfall lies very close to the Newlands and Albion springs, which are located also very close to UCT. All these similarities points to extremely local recharge zone on the lower slopes of the mountain.

Each spring has its own isotopic composition and EC value. The different isotopic compositions of the springs can be explained by their flow paths and the elevation at which recharge occurs. Each spring has its own recharge source zone. These well-defined groups could also imply that the recharge rates for the various springs are different with the less isotopically depleted springs being recharged the fastest and more isotopically depleted springs recharging more slowly. (Figure 38) show each spring recharge zone and flow path, and as previously mentioned the springs are maintained in part by the flow from the Peninsula Aquifer and the shallow Scree Aquifer.

The recharge zones position for each spring was determined by marking the highest point of each catchment which was the top of Table Mountain. The two springs in the city (De Waal and Main spring) are recharged by the rainfall that falls on the city bowl mountain side and the two springs (Newlands and Albion spring) in the southern suburbs are recharged by rainfall on the Kirstenbosch side of the mountain. From the highest point of each spring, water flows down slope towards the spring (discharge point) and the boundary lines for each zone are around small steep sloped mountain valleys where water flow down to the spring.

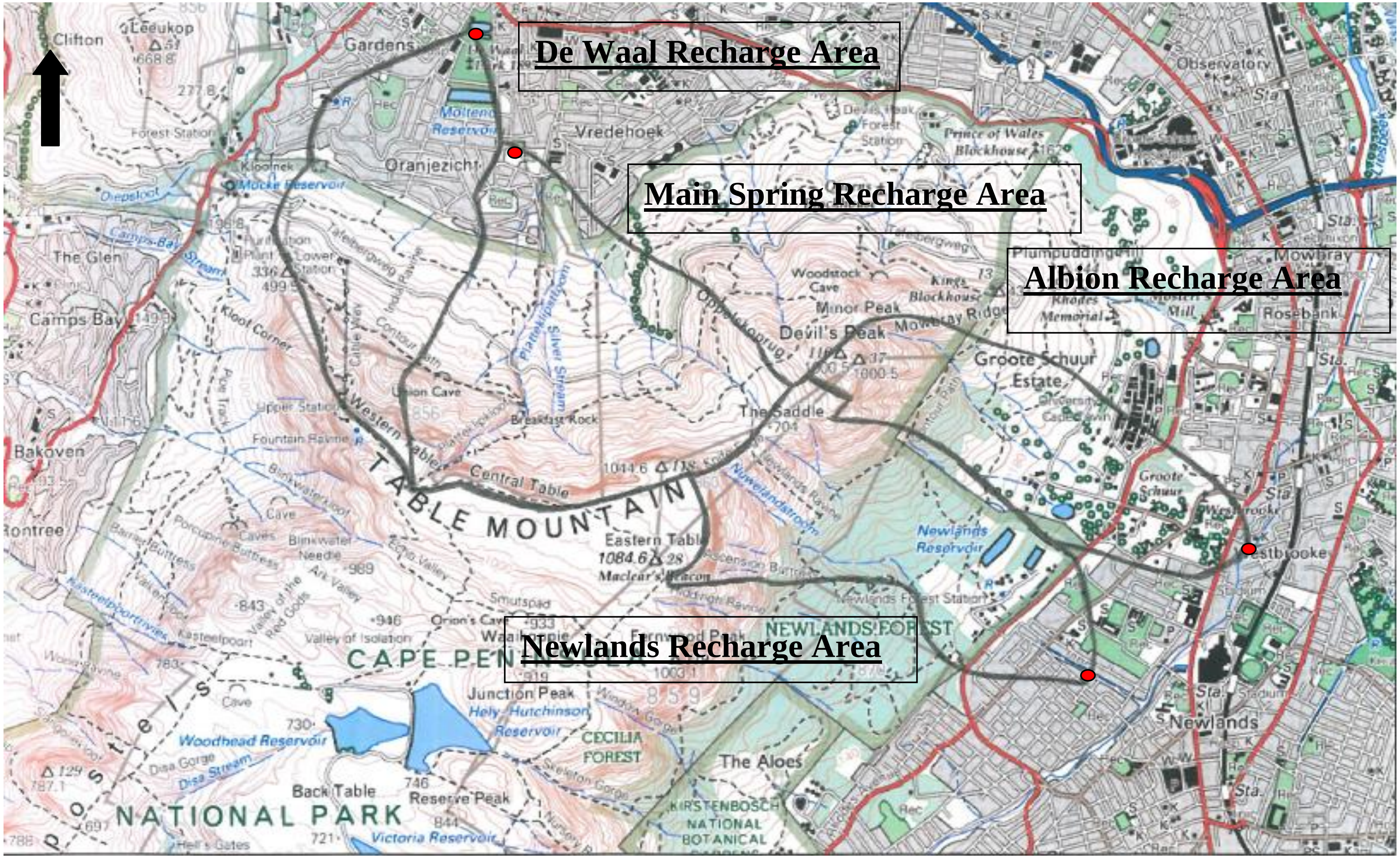


**Figure 38.** Topographic map showing the different recharge zones for each springs; the Albion spring, Newlands spring, De Waal spring and Main spring, altered map from Zondi (2014

### 5.3.2 Recharge altitude

Recharge areas with the higher average altitudes should have lower δD and $\delta^{18}O$ values. The springs distinct isotopic compositions can be explained by their recharge areas and the different altitude at which recharge occurs. (Figure 38) shows the potential recharge zones for each spring and their location on the topographic map. The average recharge altitude of each recharge zone was calculated from a topographical map of Cape Town of a 1:50000 scale, using the contour lines. For each recharge zone, a $1cm^2$ grid was constructed and the average height for each grid was estimated from the contour height in the centre of the grid. The average contour value for the grids in each recharge zone was then determined and this provides a crude estimate of the potential average altitude of recharge.

The average altitude of the potential catchment area for Albion spring is 286 m, Newlands spring is 359 m, Main spring is 518 m and for the De Waal spring is 335 m. The average recharge altitude results show that, Main spring recharge zone has got the highest average altitude and this is the spring of the lowest δD and $\delta^{18}O$ values, and the spring that is located at the highest elevation of 115 mamsl. The De Waal spring recharge zone has the lowest average altitude, has the highest δD and $\delta^{18}O$ values, and situated at an elevation of 60 mamsl, but this is not the lowest elevation of the four springs (Table 14). This reflects slight altitude effect on the isotope composition of the springs. The correlation coefficient between the springs average mean $\delta^{18}O$ and altitude is (r = -0.61) and for average mean δD and altitude is (r = -0.75), there is a strong negative correlation. It is difficult to attribute the slight isotope effect to a single factor such as altitude. The negative correlation suggests that the flow paths for the groundwater are mostly short. The lack of overlap between the different springs reveals that the springs may have different flow paths. The spring water has undergone some degree of isotopic modification maybe due to different average recharge altitude of each recharge zone. (Figure 39) shows each spring recharge zone average altitude and the average mean isotopic composition. The graph clearly shows the spring with the highest average altitude has the lowest isotope composition. The results of the average altitude shows the higher the altitude of recharge zone the longer it would take the rain water to reach the springs. There is a strong negative correlation between δD and average recharge altitude (r = -0.90) and for $\delta^{18}O$ and average recharge altitude (r = -82). Annual weighted mean $\delta^{18}O$ value of rainfall on top of Table Mountain was -4.0 ‰ in 2012, in this study De Waal spring ($\delta^{18}O$ -2.46 ‰) has a small component of mountain rainfall compared to Main spring ($\delta^{18}O$ -3.49 ‰), with Albion spring and Newlands spring in between.

**Table 14. Springs altitude, average mean δD and $\delta^{18}O$ and average recharge altitude.**

| Spring | Altitude (mamsl) | δD (‰) | $\delta^{18}O$ ( ‰) | Average recharge altitude (m) |
|---|---|---|---|---|
| Albion | 20 | -7.68 | -2.74 | 286 |
| De Waal | 60 | -6.45 | -2.46 | 335 |
| Main spring | 115 | -11.51 | -3.49 | 518 |
| Newlands | 40 | -8.44 | -3.15 | 359 |

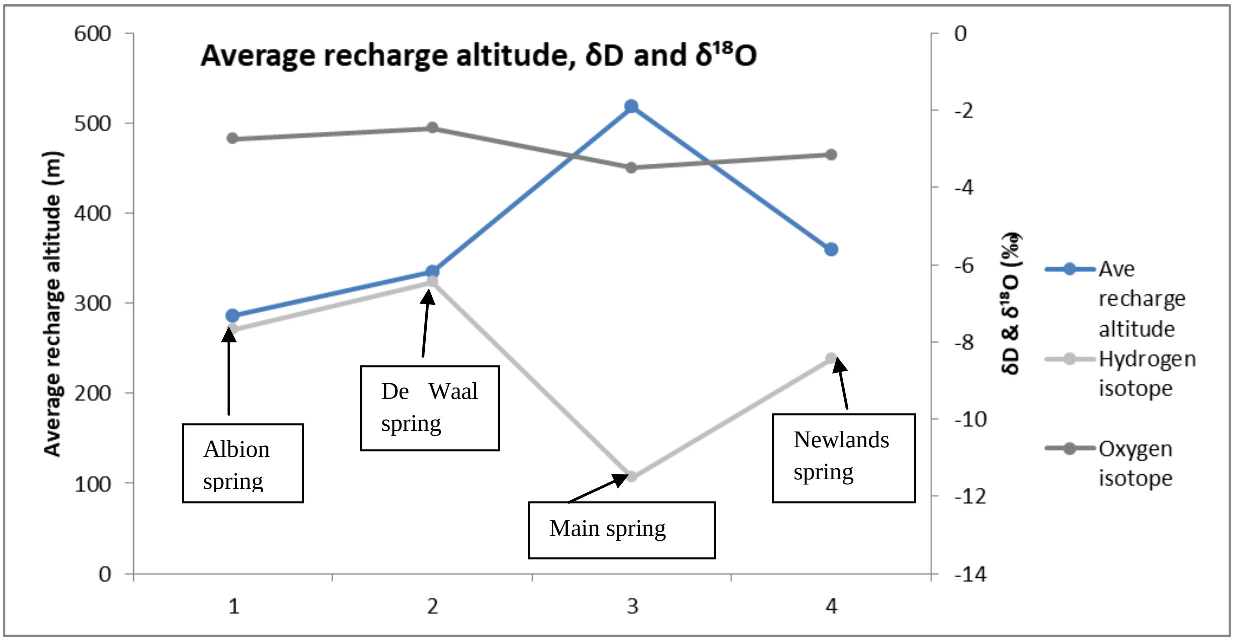


**Figure 39. Plot of the average recharge altitude, average δD and $\delta^{18}$O values of the springs.**

## 5.4 Hydrochemical characteristic

The EC in the springs' samples reflects the total dissolved ion concentrations in groundwater. Song et al. (2006) wrote that EC is one of the factors that can be used to determine the residence underground time and the length of the flow paths. The EC values of the springs range from the Albion spring with the highest average values of EC of 207µS/cm and the Newlands spring with the lowest EC values of average128 µS/cm. The EC values are not as high as to suggest there is mixing of groundwater of meteoric origin with sea-water. As described in the results section there is no correlation between springs' altitude and the springs EC values. Albion spring is situated at the lowest altitude and has the highest EC values. This could have been interpreted as; the spring that lays the furthest from the start of the recharge zone might have the highest EC values, because of the long flow path. The main spring is situated at the highest elevation among the springs, resulting in short flow path, but does not have the lowest EC values (Table 12). This lack of correlation means that the slight range in EC of these springs is not generally due to the great distance between the start of recharge zone and the discharge point. This also means that the residence time of the groundwater must be short.

Depleted isotopic signature and low electrical conductivity indicate a lower evaporation rate exists. Newlands spring has got the lowest EC values and has got the second most depleted isotopic signatures. This could reflect the fact that the spring water was impacted by evaporation before recharge. Newlands has the lowest EC values and it is situated at 40 mamsl, this suggests a short flow path along the mountain slope with a relatively short residence time, but Newlands spring is not situated at the highest altitude to other springs. Main spring is situated at the highest altitude with higher EC values than Newlands spring. The highest EC for groundwater was found at Albion spring, where the d-excess average value is the second lowest at 14.22. Main spring has got the second highest EC values and situated at the highest altitude, this could possibly indicate a relatively long residence time for groundwater at this site.

Albion spring has the highest EC and has the most industries in catchment area, but there is no published information by fertilizers, sewage, and acid deposition at the Albion area. The EC values of the springs could reflect geology or soil specific to their recharge site. Recent samples from the springs were analysed for microchemistry, to see which element might contribute to the EC values in the springs water. Maybe natural attenuation of nitrate (i.e., denitrification) has occurred in the Albion spring area. Liu & Yamanaka (2010) was able to show by a trilinear diagram from cation and anion concentration results in his study area that Ca-$HCO_3$ was the dominant hydrochemical facies that contributed to the high EC values. He did the hydrochemical analyses by measuring the bicarbonate concentration by the titration method using sulfuric acid.

Water samples from the four springs for the months of January and February 2017 were analysed for trace constituents using the ICP-MS. Major cations (Na, Cl, Mg, etc) could not be determined, as the Department of Geological Sciences does not have the facilities to determine Na, Cl etc. Many of the concentrations are very low, but there are some consistent differences between the springs, (Table 15). Albion spring had the highest elements concentrations among the four springs. It was hoped that these results (low-concentrations metals) could provide additional information to explain the reason for the different in the EC values between the springs, but Major cations would have been more applicable in this problem. Rosewarne (2002) wrote that groundwater in the Table Mountain Group has got low pH, which results in minerals readily dissolving, because they all have similar low pH and they have overall low EC.

**Table 15. Springs microchemistry data analysed by using ICPMA.**

| Springs microchemistry data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Element | De Waal | Newlands | Main spring | Albion | De Waal | Newlands | Main spring | Albion |
| (ppb) | Jan 2017 | Jan 2017 | Jan 2017 | Jan 2017 | Feb 2017 | Feb 2017 | Feb 2017 | Feb 2017 |
| Sc | 1.01 | 1.35 | 1.42 | 1.60 | 1.04 | 1.35 | 1.30 | 1.66 |
| Ni | 15.18 | 2.83 | 6.28 | 34.52 | 1.87 | 2.08 | 4.92 | 28.1 |
| Cu | 3.08 | 2.26 | 2.84 | 91.79 | 3.98 | 2.56 | 4.43 | 544.6 |
| Zn | 11.43 | 10.54 | 18.85 | 593.50 | 18.16 | 11.82 | 26.17 | 2977.0 |
| Rb | 2.17 | 4.25 | 4.58 | 4.04 | 2.13 | 3.96 | 4.32 | 4.0 |
| Sr | 27.14 | 20.38 | 19.36 | 43.41 | 27.26 | 20.74 | 19.30 | 42.3 |
| Ba | 2.40 | 18.46 | 16.93 | 22.43 | 1.92 | 18.65 | 17.25 | 22.6 |
| V | 0.63 | 0.67 | 0.94 | 0.86 | 0.66 | 0.69 | 0.83 | 0.80 |
| Cr | 0.54 | 0.57 | 0.71 | 0.69 | 0.58 | 0.67 | 0.66 | 0.83 |
| Ga | 0.12 | 0.49 | 0.42 | 0.53 | 0.05 | 0.50 | 0.44 | 0.6 |
| Y | 0.25 | 0.04 | 0.03 | 0.07 | 0.27 | 0.02 | 0.32 | 0.1 |
| Zr | 0.65 | 0.79 | 0.90 | 1.13 | 0.83 | 0.75 | 0.83 | 1.0 |
| Er | 0.08 | 0.03 | 0.01 | 0.01 | 0.03 | 0.003 | 0.023 | 0.004 |
| Yb | 0.08 | 0.03 | 0.01 | 0.01 | 0.03 | 0.003 | 0.027 | 0.007 |
| Hf | 0.09 | 0.05 | 0.02 | 0.03 | 0.01 | 0.019 | 0.013 | 0.018 |
| Pb | 0.63 | 0.48 | 0.87 | 9.80 | 0.77 | 0.129 | 0.518 | 16.58 |
| Th | 0.09 | 0.03 | 0.01 | 0.01 | 0.01 | 0.002 | 0.003 | 0.004 |
| U | 0.16 | 0.05 | 0.02 | 0.02 | 0.06 | 0.003 | 0.047 | 0.003 |

There is no correlation between the springs EC values and the water temperature, altitude and the isotope composition. If a spring has the highest EC, and the d-excess values are the lowest, this indicates an evaporation enrichment effect. The different springs plot in distinct fields that are isotopically different from one another, with Main spring having the lowest $\delta D$ and $\delta^{18}O$ values, Albion and Newlands spring with an intermediate isotopic composition and De Waal spring having the highest $\delta D$ and $\delta^{18}O$ values. Each spring has its own range EC values; this supports the conclusion that the recharge water for each spring is derived from different pathways.

# Chapter 6 Conclusions

The line of best fit from the monthly rainfall data calculated using the reduced major axis method suggest a local meteoric water line (LMWL) with the equation $\delta D = 6.03*\delta^{18}O + 7.07$. This is similar to the previously calculated equation with the dataset from 1995-2008. There is a strong seasonal effect, which is mostly driven by amount and temperature effect. The summer and winter months' data show there is a clear seasonal difference in the isotope composition. If the springs' isotope data reflect the same seasonal effect as the rainfall, this show that the rainfall is the source of the spring recharges water but due to mixing of rainfall water taking place during recharge, the composition of discharge is average out. The similarities in the isotopic composition of the springs' $\delta D$ and $\delta^{18}O$ values from year to year can be interpreted as rainfall water mixing with water in the aquifer. The springs plot in distinct fields that are isotopically different from one another, with Main Spring having the lowest $\delta D$ and $\delta^{18}O$ values, Albion and Newlands spring with an intermediate isotopic composition and De Waal spring has got the highest $\delta D$ and $\delta^{18}O$ values. Each spring has its own EC signature; this supports the conclusion that the recharge water for each spring is derived from different flow paths.

The change in the springs' d-excess values clearly mimics that of the rainfall, whereas $\delta D$ and $\delta^{18}O$ values on their own tend to be ambiguous, d-excess values can support the findings of the $\delta D$ and $\delta^{18}O$ values, this is observed in the data produced in the Tables. The similar pattern changes of the d-excess values and $\delta D$ and $\delta^{18}O$ of the rainfall is reflected in the spring water at a short period, suggesting that recharge is occurring rather rapidly and from the d-excess values, the recovery seem to occur from month to month for some springs. This is inferred as with every monthly change in the rainfall d-excess values, the springs d-excess values also changes. The De Waal spring is recharged the fastest, recovery occurs from month to month. Newlands d-excess does not change at the same time at the rainfall's d-excess, Newlands is the slowest spring to recover, with recharge occurring at least within three months. Main spring and Albion spring fall in between the fastest and slowest recovering spring. The springs are recharged at different rates but with the general average of recharge rate of one to three months recovery.

The springs are recharged by rainfall and the winter rainfall seems to be the main source of the spring recharge. An explanation for the rapid recharged is explained by the combination of rainfall that recharges the Peninsula Aquifer and the shallow Scree Aquifer. Recharge from the Scree Aquifer is a lot more rapid than the Peninsula Aquifer, but the Peninsula Aquifer support the Scree Aquifer to maintain recharge occurring on a yearly basis. The average altitude results show that, Main spring recharge zone has got the highest average altitude; Main spring also has the lowest isotope composition among the four springs, while De Waal spring recharge zone has the lowest average altitude and has the highest isotope composition. This reflects the altitude effect on the isotope composition of the springs. Annual weighted mean $\delta^{18}O$ value of rainfall on top of Table Mountain was -4.0 ‰, therefore De Waal spring ($\delta^{18}O$ -2.46 ‰) has a small component of mountain rainfall compared to Main spring ($\delta^{18}O$ -3.49 ‰), with Albion spring and Newlands spring in between.

EC values is distinct for each spring throughout time of sampling, there is no overlap at all. This must be related to substrate, as there is no correlation between springs EC values with the springs' altitude and isotope composition. This lack of correlation means that the slight range in EC of these springs is not generally due to the great distance between the start of recharge zone and the discharge point (spring).

## Recommendations:

Total dissolved solids (TDS) should be one of the parameters measured to help determine the quality of the water. Major cations (Na, Cl, Mg, etc) should be measured to determine which element might be contributing to the EC values in the springs' water. There is no recent data available for the springs' yields. The springs' yields should be measured while sampling to determine each spring's yield and see if the yields change with the different seasons. There is potential to further the study and continue comparing rainfall composition to the springs to see if there is any change in the recharge rates over a period of drought. The difference between the Peninsula Aquifer water and the Scree Aquifer water should be determined, to see when the different aquifers water recharge the springs'.

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# Appendix: Microchemistry data analysed by using ICPMA.

| Isotope | Element | De Waal | %RSD | Newlds | %RSD | Main | %RSD | Albion | %RSD | DeWaal | %RSD | Newlds | %RSD | Main | %RSD | Albion | %RSD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ppb | Jan 2017 | | Jan 2017 | | Jan 2017 | | Jan 2017 | | Feb 2017 | | Feb 2017 | | Feb 2017 | | Feb 2017 | |
| 7Li | Li | 0.62 | 17.6 | 0.90 | 0.9 | 1.15 | 0.4 | 1.03 | 7.7 | <d.l. | | 0.45 | 14.4 | 0.62 | 2.6 | 0.52 | 3.8 |
| 45Sc | Sc | 1.01 | 0.7 | 1.35 | 0.0 | 1.42 | 5.2 | 1.60 | 1.6 | 1.04 | 1.9 | 1.35 | 1.3 | 1.30 | 1.5 | 1.66 | 0.8 |
| 51V | V | 0.63 | 1.5 | 0.67 | 2.5 | 0.94 | 0.1 | 0.86 | 3.5 | 0.66 | 6.2 | 0.69 | 1.2 | 0.83 | 1.2 | 0.80 | 0.0 |
| 52Cr | Cr | 0.54 | 4.9 | 0.57 | 2.8 | 0.71 | 0.3 | 0.69 | 2.2 | 0.58 | 1.5 | 0.67 | 5.8 | 0.66 | 5.3 | 0.83 | 2.5 |
| 59Co | Co | <d.l. | | <d.l. | | <d.l. | | <d.l. | | <d.l. | | <d.l. | | <d.l. | | <d.l. | |
| 60Ni | Ni | 15.18 | 0.1 | 2.83 | 1.0 | 6.28 | 1.0 | 34.52 | 1.3 | 1.87 | 6.4 | 2.08 | 3.4 | 4.92 | 0.9 | 28.1 | 0.6 |
| 65Cu | Cu | 3.08 | 2.2 | 2.26 | 0.3 | 2.84 | 1.3 | 91.79 | 0.4 | 3.98 | 1.0 | 2.56 | 1.6 | 4.43 | 1.8 | 544.6 | 0.6 |
| 66Zn | Zn | 11.43 | 1.2 | 10.54 | 1.1 | 18.85 | 1.1 | 593.50 | 0.5 | 18.16 | 0.2 | 11.82 | 0.2 | 26.17 | 1.1 | 2977.0 | 0.7 |
| 69Ga | Ga | 0.12 | 4.3 | 0.49 | 0.3 | 0.42 | 0.4 | 0.53 | 0.0 | 0.05 | 4.0 | 0.50 | 1.1 | 0.44 | 2.6 | 0.6 | 0.9 |
| 85Rb | Rb | 2.17 | 1.7 | 4.25 | 1.4 | 4.58 | 1.1 | 4.04 | 0.9 | 2.13 | 2.1 | 3.96 | 1.3 | 4.32 | 1.7 | 4.0 | 1.2 |
| 88Sr | Sr | 27.14 | 0.5 | 20.38 | 0.4 | 19.36 | 0.7 | 43.41 | 0.7 | 27.26 | 1.2 | 20.74 | 1.2 | 19.30 | 0.9 | 42.3 | 0.9 |
| 89Y | Y | 0.25 | 7.9 | 0.04 | 9.8 | 0.03 | 5.7 | 0.07 | 3.2 | 0.27 | 1.5 | 0.02 | 4.2 | 0.32 | 0.9 | 0.1 | 12.0 |
| 90Zr | Zr | 0.65 | 1.8 | 0.79 | 1.7 | 0.90 | 3.1 | 1.13 | 0.3 | 0.83 | 0.2 | 0.75 | 4.5 | 0.83 | 2.5 | 1.0 | 1.4 |
| 93Nb | Nb | 0.26 | 8.0 | 0.11 | 1.4 | 0.07 | 5.8 | 0.04 | 8.0 | 0.02 | 11.1 | 0.02 | 13.9 | 0.01 | 12.9 | 0.0 | 19.1 |
| 133Cs | Cs | 0.31 | 2.3 | 0.55 | 1.4 | 0.47 | 0.8 | 0.53 | 2.2 | 0.19 | 5.8 | 0.43 | 2.0 | 0.45 | 0.7 | 0.5 | 0.5 |
| 137Ba | Ba | 2.40 | 2.9 | 18.46 | 0.3 | 16.93 | 0.6 | 22.43 | 0.8 | 1.92 | 1.2 | 18.65 | 0.8 | 17.25 | 0.1 | 22.6 | 0.9 |
| 139La | La | 0.59 | 2.3 | 0.03 | 3.0 | 0.01 | 10.7 | 0.01 | 8.6 | 0.71 | 2.8 | <d.l. | | 0.01 | 17.1 | <d.l. | |
| 140Ce | Ce | 1.12 | 2.4 | 0.03 | 4.6 | 0.01 | 47.0 | 0.01 | 8.2 | 1.53 | 0.9 | <d.l. | | 0.01 | 0.2 | 0.002 | 11.7 |
| 141Pr | Pr | 0.18 | 4.2 | 0.03 | 1.5 | 0.01 | 1.3 | 0.01 | 5.3 | 0.18 | 4.2 | 0.001 | 19.8 | 0.00 | 19.7 | <d.l. | |
| 144Nd | Nd | 0.53 | 1.2 | 0.03 | 26.6 | 0.02 | 2.6 | 0.01 | 12.8 | 0.73 | 1.4 | <d.l. | | 0.00 | 47.9 | <d.l. | |
| 152Sm | Sm | 0.14 | 5.6 | 0.02 | 2.5 | 0.01 | 4.4 | 0.00 | 39.2 | 0.13 | 1.1 | <d.l. | | <d.l. | | <d.l. | |
| 153Eu | Eu | 0.10 | 2.2 | 0.03 | 3.3 | 0.01 | 2.3 | 0.01 | 8.8 | 0.03 | 3.6 | <d.l. | | <d.l. | | <d.l. | |
| 159Tb | Tb | 0.08 | 13.4 | 0.03 | 0.2 | 0.01 | 20.5 | 0.01 | 14.2 | 0.02 | 11.2 | 0.002 | 23.5 | 0.003 | 4.1 | <d.l. | |
| 160Gd | Gd | 0.14 | 9.0 | 0.02 | 14.3 | 0.01 | 46.9 | 0.01 | 30.1 | 0.11 | 2.8 | <d.l. | | 0.009 | 14.9 | <d.l. | |
| 163Dy | Dy | 0.13 | 8.0 | 0.03 | 2.1 | 0.01 | 3.8 | 0.01 | 13.6 | 0.08 | 0.0 | <d.l. | | 0.026 | 2.9 | 0.003 | 48.6 |
| 165Ho | Ho | 0.09 | 7.5 | 0.03 | 10.1 | 0.01 | 7.8 | 0.01 | 8.2 | 0.02 | 4.2 | 0.002 | 28.0 | 0.007 | 11.6 | <d.l. | |
| 166Er | Er | 0.08 | 15.3 | 0.03 | 2.2 | 0.01 | 23.5 | 0.01 | 21.1 | 0.03 | 2.2 | 0.003 | 30.5 | 0.023 | 3.3 | 0.004 | 11.5 |
| 169Tm | Tm | 0.07 | 15.9 | 0.03 | 1.6 | 0.01 | 4.3 | 0.00 | 1.4 | 0.01 | 5.2 | 0.002 | 1.5 | 0.004 | 6.5 | <d.l. | |
| 174Yb | Yb | 0.08 | 9.9 | 0.03 | 4.0 | 0.01 | 18.3 | 0.01 | 8.3 | 0.03 | 1.8 | 0.003 | 15.0 | 0.027 | 2.7 | 0.007 | 18.0 |
| 175Lu | Lu | 0.09 | 15.0 | 0.03 | 2.4 | 0.01 | 13.9 | 0.01 | 16.8 | 0.01 | 3.5 | 0.001 | 22.6 | 0.004 | 9.3 | <d.l. | |
| 178Hf | Hf | 0.09 | 0.7 | 0.05 | 3.3 | 0.02 | 2.8 | 0.03 | 2.5 | 0.01 | 14.8 | 0.019 | 3.5 | 0.013 | 5.6 | 0.018 | 2.9 |
| 181Ta | Ta | 0.12 | 11.3 | 0.04 | 6.4 | 0.02 | 4.7 | 0.01 | 9.8 | 0.01 | 4.9 | 0.001 | 10.8 | <d.l. | | <d.l. | |
| 208Pb | Pb | 0.63 | 2.8 | 0.48 | 1.1 | 0.87 | 1.2 | 9.80 | 0.6 | 0.77 | 1.5 | 0.129 | 2.6 | 0.518 | 2.3 | 16.58 | 0.8 |
| 232Th | Th | 0.09 | 6.2 | 0.03 | 7.6 | 0.01 | 15.5 | 0.01 | 3.2 | 0.01 | 22.1 | 0.002 | 4.3 | 0.003 | 15.1 | 0.004 | 21.8 |
| 238U | U | 0.16 | 11.0 | 0.05 | 4.8 | 0.02 | 10.9 | 0.02 | 18.5 | 0.06 | 6.1 | 0.003 | 9.7 | 0.047 | 5.1 | 0.003 | 11.9 |