APPLICATION OF ENVIRONMENTAL TRACER METHODS TO CONCEPTUALIZE GROUNDWATER RECHARGE, WEST COAST, SOUTH AFRICA

Environmental and Water Science in the Department of Earth Science

Faculty of Natural Sciences at the University of the Western Cape

By

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Declaration

I declare that *Application of environmental tracer methods to conceptualise groundwater recharge, West Coast, South Africa* is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete reference.

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Abstract

Drought and climate change will have adverse consequence for freshwater resources in water stressed South Africa. Diminishing surface water reserves increases the demand to exploit groundwater resources. The drought conditions experienced in South Africa in 2016 is exacerbated in semi-arid portions of the Western Cape, where freshwater resources are further limited. Traditional physical methods are proven to be inadequate in semi-arid and arid regions due to difficulties in accurate measurements of variables for recharge studies. Geochemical methodologies have become more attractive for recharge investigations in drought prone hydrogeological environments due to natural labeling of water throughout the hydrological cycle. Quantitative and qualitative information on aquifer recharge rates and mechanism are needed to manage groundwater resources in the West Coast. Therefore, the aim of this study is to design a hydrogeological conceptual model which describes recharge mechanism and estimates recharge by using combined environmental tracer techniques in coastal aquifer system, using the West Coast Aquifer System as a case study. Groundwater of the upper unconfined aquifer, confined Langebaan Road Aquifer Unit and the Elandsfontein Aquifer Unit, surface water and rainwater samples (n=239) were collected on a quarterly basis during wet winter season (May and August 2017) and dry summer season (November 2017 and February 2018) for stable isotopes and chloride. Tritium and carbon-14 were sampled at selected groundwater monitoring sites (n=31) once during the data collection period.

The analysis of groundwater in the unconfined and confined units revealed a similar $\delta^{18}O$‰ and $\delta^{2}H$‰ values which suggests that all aquifer units have the same source of recharge which could possibly be rainfall but at different locations which correlates well with previous stable isotope investigations in the study area. The results revealed that the Berg River is a gaining stream due to significant differences in isotopic composition compared to groundwater. The study also revealed that groundwater at Geelbek Lagoon is not of the same groundwater system as the EAU due to its highly enriched stable isotopic composition which is supported by elevated chloride concentration. This led to the identification of a freshwater/saline water interface in the vicinity of the Geelbek Lagoon. The spatio-temporal assessment of stable isotopes revealed that change in isotopic composition shows a strong relationship with seasonality and amount, as groundwater mimics isotopic composition and evaporation effects of infiltrating in a particular season. This suggests

that recharge occurred during the wet winter months and that recharge mechanism is direct and immediate for the unconfined aquifer. Moreover, stable isotope composition of groundwater sampled from bedrock aquifer revealed temporal changes in isotopic composition. When coupled with depth of boreholes suggest that the source of recharge experiences evaporation effects and that recharge mechanism is direct via preferential flow paths such as faults and fractures.

Using Clarke and Fritz's' (1997) qualitative assessment for groundwater tritium in coastal and low latitudes revealed groundwater tritium activities for the WCAS at 0.0-1.2T.U. The highest tritium activities were measured in an agricultural area in the middle portion of the aquifer, eastward and downgradient from the recharge zone, which suggests that portion of modern recharge could be attributed to irrigation return flow. Tritium activities seems to be highest at boreholes that were measured along the inferred Malmesbury-Granite contact. Tritium activity of the middle of the LRAU (0.8T.U) and in the basal aquifer (0.7 T.U) at the Langebaan Road Wellfield are the highest for groundwater for the confined aquifer. The locality of elevated tritium activity coupled with borehole depth, location of the inferred contact suggests that a focused recharge mechanism via fractures and faults to the basement and LRAU occurs. This result is supported by the immediate change is stable isotopes values for the basal aquifer which are enriched during the onset of the wet winter season and depleted after the rainy season. The result for the groundwater in the middle of LRAU shows an increase of 0.7 from 2002 when tritium activity was measured at 0.1T.U. This suggests that the borehole casing at this site could be leaking to produce the elevated tritium results from this study.

Groundwater residence times were calculated using radiocarbon values sampled from unconfined, confined and basal aquifers. Overall groundwater radiocarbon content correlate well with borehole depth as deep groundwater showed longer residence times than shallow groundwater. Carbon-14 content was highest at boreholes close to the coast with high pMC content (BH2=59.pMC; G46060=61.2 pMC). The high pMC content coupled with the deposition of thick calcrete deposits suggests that water-rock interaction occurs. The high pMC values indicate that recharge occurred close to 1952 in the peak of the ^{14}C due to bomb testing. However, this is not supported by the tritium activity at the Geelbek Lagoon where tritium activity was measured at 0.0T.U. The close proximity of the ocean and the lagoon coupled with high ^{14}C content, enriched stable isotope composition, hypersaline chloride concentration and low tritium activity suggests that groundwater was not recharged recently and that water-rock reactions occur between groundwater and calcrete occur due to thick calcrete lenses. This implies that a subterranean estuary exists close at Geelbek Nature Reserve and that groundwater is direct interaction with either the Atlantic Ocean and/or Geelbek Lagoon. The measured pMC content of groundwater samples which penetrate both unconfined and confined aquifers at the same location were significantly different which suggests that the clay aquitard is thickest at that location and that is little interaction between the upper aquifer and the lower confined aquifer.

Application of the Chloride Mass Balance (CMB) technique to the unconfined aquifer unit showed that groundwater recharge was estimated at 5.15mm which represents 3.25% of the total mean annual rainfall for the West Coast. These estimates correlate well with previous estimates yielded from physical and chemical methodologies, when the decreased rainfall of 2017 is considered. Site specific results revealed that the unconfined aquifer is recharged throughout the study area from rainfall, while the recharge area was delineated in the high lying area close to Hopefield.

Future predictions by the IPCC suggest that for coastal aquifers in semi-arid are threatened by increased temperature, decreased rainfall and sea level rise. The conceptualization of groundwater recharge using environmental isotopes has illustrated that the WCAS, especially the southern portion of the EAU is threated by salinization. Overall, the robust geochemical methodology applied in this study can be used to conceptualize groundwater system at regional scale and can be applied to other hydrogeological coastal environments. The findings of this research can also contribute to short rather than long term management of coastal aquifers.

Acknowledgements

I am grateful and blessed to have the opportunity to pursue a master's degree of any kind. I stand on the shoulders of many people that have broken their backs so that I could be willing to be afforded this opportunity. To my parents I would like to extend my gratitude for your never-ending support. I hope that one day my shoulders are strong enough to support you.

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Chapter 1- General Introduction

1.1 Introduction

The supply of freshwater on Earth is entirely due to the existence of the global hydrological cycle (Pokorný, 2005). Freshwater quantity and quality availability are a prerequisite for food security, animal health, ecosystem protection, thus making water essential for life on earth (Pokorný, 2005). Today, many regions of the world face the challenge of declining water supplies due to increasing demand for water resources due to population and income growth (Mancosu et al, 2015). The shortage of good quality water from rivers and lakes to has made groundwater an important source of drinking water in many urban settlements. Since recharge is the primary hydrological process through which water enters an aquifer, understanding the process is important in securing supply of freshwater.

Recharge has been defined as "the entry into the saturated zone of water made available at the water-table surface, together with the associated flow away from the water table within the saturated zone" (Freeze and Cherry 1979). This may occur naturally from precipitation, rivers, canals and lakes, and man-induced through activities of irrigation and urbanization. Determining recharge is the most important aspect of hydrological system. However, recharge estimation remains one of the biggest challenges for groundwater investigators due to the complexity in estimation. Therefore, the occurrence of recharge estimates approximates the amount of water which enters the groundwater system which is difficult to measure accurately (Adams, 2004; Scanlon *et al*, 2002). An approximation of recharge rates is imperative for the effective management and protection of valuable and limited groundwater resources in semi-arid regions. Consequently, the understanding of the mode of recharge, factors controlling recharge processes and the estimation are essential for improving water resources management (Healy, 2010).

Conceptual models are essential illustrative tool developed to represent a system to improve knowledge and understanding of the system and simulate processes within the system (Healy, 2010; Scanlon *et al* 2002). The benefits of developing a conceptual understanding of groundwater recharge processes and mechanisms are vital when ensuring sustainable management practices of groundwater in a system. In order to secure groundwater resources, a conceptual understanding of groundwater recharge processes, recharge mechanisms and groundwater/rainfall interactions is needed. An effective conceptual groundwater recharge model can influence institutional arrangements significantly to improve management abstraction and water allocation in an area.

1.2 Background

In 1985 Timmerman conducted ground-breaking work which is still being used to date to describe the hydrogeology in the West Coast. Timmerman's research provided the first real glimpse into regional characterization of aquifers from Yzerfontein to Aurora. The report is the first to delineate the four primary aquifers in the West Coast namely; the Grootwater, Elandsfontein, Langebaan Road and Adamboerskraal Aquifers (Timmerman, 1985(KMG); Timmerman, 1985 (a,b,c). The report is the first to provide a description of the unconfined upper aquifer unit (UAU), clay aquitard confined lower aquifer unit (LAU). According to Timmerman regionally the UAU is unconfined and the aquifer lies within the Cenozoic sands of the Sandveld Formation and recharge to the aquifer occurs directly from precipitation. The main aquitard which separates the UAU and LAU is deposited discontinuously and composed of clay of the Elandsfontein formation. The aquitard of the Grootwater Aquifer (GA) differs from the Elandsfontein (EA), Langebaan Road Aquifer (LRA) and Adamboerskraal Aquifer (AAU) in that it is not composed of clay of the Elandsfontein formation, but from muddy peat layering of the Duynefontein formation. The LAU of the EAU, LRAU and AAU is mainly composed coarse shelly gravel of the Elandsfontein formation whereas the LAU of the GA is composed of quarzitic sand of the Varswater Formation. Metasediments of the Malmesbury Group forms the regional geological basement of the study area, with intrusions of the Cape Granite Suite occurring locally throughout the study area.

Historically, the Elandsfontein and Langebaan Road Aquifers are by far the most studied of the four primary aquifers in the West Coast (Vermaak, 2013). The Grootwater and Adamboerskraal aquifers have been greatly neglected, although groundwater from these aquifers is being used by for domestic supply and agricultural production. More recently in 2016, the South African government has declared drought conditions for portions of the country, the West Coast being one of those areas. The region experiences the lowest rainfall per annum throughout the Western Cape and the recent drought has reduced the amount of water that adds to the saturated zone. The drought was caused by the El Niño-Southern Oscillation which is the main driver for drought conditions in the Western Cape (Eilers, 2017; Lian et al, 2017). The El Niño event of 2015/2016 has one of the strongest recorded in history which would alter global air circulation and rainfall patterns.

The West Coast District Municipality (WCDM) which includes the towns of Saldanha, Langebaan and Hopefield is north of Cape Town which has the distinction of being the first metropolitan city in the world that could not have water to supply for its residents. The WCDM and Cape Town forms the Western Cape Water Supply System (WCWSS). The WCDM is the last to receive water from the WCWSS which why current attempts are being made to use groundwater to relieve the pressure on surface water supply. Groundwater is used in the West Coast for agriculture from stock watering, municipal and industrial use. In 1999 the West Coast District Municipality commissioned a wellfield for the supply to Saldanha Bay Municipality was licensed to abstract 1.46 million m^3 of groundwater per annum form the at the Langebaan Road Aquifer Unit (LRAU). During the operation of this wellfield there have been adverse impacts on groundwater reserves as water levels have declined between 10-11 metres from pre-wellfield days (Clarke *et al*, 2018). Increased industrial activity and population growth has increased pressure on water resources in the area.

1.3 Description of research problem

The traditional and most common method to conceptualize and characterize groundwater recharge is by using physical methods which provide direct measurements to assess the hydraulic nature of an aquifer (Diamond, 2014). This is done by using water level and pressure measurements taken from boreholes that penetrate the aquifer being investigated. These measurements are minute in semi-arid regions making it difficult to apply physical recharge methods accurately (Healy, 2010). Groundwater levels in the West Coast Aquifer System behaviour varies regionally throughout the aquifer and a single direct measurement is not representative of the regional flow dynamics that occur within the groundwater system (Seyler *et al*, 2017). Exacerbated by drought that the Western Cape experienced in 2016 and 2017, direct measurements used to characterise groundwater recharge through the application of physical measurements would have been even more erroneous and inaccurate than ever before. The application of geochemical methods is attractive in semi-arid regions and offer a solution to characterise groundwater recharge an elucidate groundwater flow in an aquifer (Grismer *et al*, 2000; Scanlon *et al*, 2002). Geochemical methods provide an alternative to physical methods to quantitatively and qualitatively conceptualize groundwater recharge as the chemical nature of groundwater varies regionally with altitude and is provides and advantage over physical methods as they are cheaper.

Literature focusing on recharge investigations has evidenced that the use of geochemical methods is suitable to quantify recharge and distinguish sources of recharge zones in semi-arid regions. However, there has been lack of use of this method to describe hydrogeological conceptual models (Kpegli, 2018). Successful application of geochemical methods such as environmental isotope techniques and Chloride Mass Balance method has been successfully applied in coastal semi-arid regions globally to estimate groundwater recharge, establish sources of recharge and groundwater residence time (Weaver & Talma, 2005; Conrad *et al*, 2004; Adams, 2004; Eilers, 2018).

Implementation of geochemical methods to provide knowledge of the recharge systems needs to be investigated in the West Coast as a comprehensive regional understanding of the hydrosystem, as well as recharge is lacking. In semi-arid regions where recharge estimates are generally low, the implementation of a geochemical approach to provide understanding of recharge is important, as actual recharge is inversely proportional to concentration of chemical constituents present in groundwater (Scanlon *et al*, 2002). In South Africa, laboratory methods used to detect exact concentration of elements present in water have advanced significantly (Clarke *et al*, 2018). Through innovative laboratory methods, geochemical methods can be used to provide insight into recharge mechanisms, regardless of the amount of water that has been added to the groundwater reservoir.

Groundwater recharge has received a lot of attention in South Africa (Xu and Beekman, 2003). However, limited studies focus on groundwater recharge for the West Coast Aquifer System. Due to limited and fragmented geochemical (environmental isotope) data for the study area makes it difficult to accurately quantify and conceptualize groundwater recharge. While some studies have focused on one or two environmental isotopes, there is limited studies that apply a multiple environmental isotope approach to conceptualize groundwater recharge to the West Coast Aquifer System. While some studies have used secondary data to model recharge for hydrogeological units in the West Coast, there are limited studies that used primary hydrochemical data to quantify and conceptualize groundwater recharge in the West Coast.

1.4 Research question and thesis statement

1.4.1 Research question

How appropriate is the use of environmental tracers to develop a hydrogeological conceptual model focusing on groundwater recharge in coastal hydrogeological environment?

1.4.2 Thesis statement

The central argument is that if the hydrochemistry of hydrological inputs in a semi-arid, drought prone coastal aquifer is understood, then the hydrogeological regional recharge conceptual model can be designed using geochemical methods without the use of conventional physically based methods.

1.5 Research aim and objectives

1.5.1 Aim

The study is aimed to characterise groundwater recharge of coastal aquifers using a geochemical approach by applying the methodology to the West Coast Aquifer System as a case study. The geochemical data will be used to design a hydrogeological conceptual model which constrains sources of recharge to the WCAS and quantifies recharge to the UAU using the Chloride Mass Balance technique. This study aims to produce a contemporary conceptual model that could be used to inform effective groundwater management strategies in the West Coast.

1.5.2 Objectives

1. Establish groundwater recharge sources, flow and mixing processes to explain recharge mechanism by using multiple environmental isotopes.
2. Estimate annual groundwater recharge to unconfined aquifer using Chloride Mass Balance Method.
3. Design a hydrogeological recharge conceptual model for the WCAS

1.6 Significance of the study

Groundwater is integral part of the hydrologic system, but it is only in the last few decades that awareness of its limited supply is known. Recently groundwater management interventions have been promulgated to protect this valuable resource. Understanding groundwater recharge is essential for the successful management of water resources. This is especially important in semi-arid regions, where mean annual precipitation is significantly lower than the global rainfall average .Moreover, contemporary recharge investigations are important in South Africa as water resources are considerably less. Knowledge of the rate at which water in an aquifer system is replenished is critical for the assessment of groundwater availability. Groundwater is life sustaining resources that is important for human livelihoods as well as healthy ecosystem functioning.

Groundwater recharge investigation are vital as recharge processes act in opposition to discharge processes, so the relative magnitudes of recharge give an indication of the health of an aquifer. Where contamination of an aquifer is a concern, estimating the recharge rate is a first step toward predicting the rate of solute transport to the aquifer. Through investigation of recharge, distinguishing recharge areas are critical in managing land use activities, as those activities that could potentially contaminate the aquifer, are controlled or stopped. Utilizing methods such as chloride mass balance and environmental isotopes is crucial, since these methods are suitable and practical approaches to estimate groundwater recharge. These techniques provide insight into recharge mechanisms that enables the prediction of groundwater availability to inform practical strategies for best management practice of groundwater resources.

1.7 Research Framework

The study is aimed at understanding the spatio-temporal activities of environmental tracers of different hydrogeological units of the West Coast Aquifer System in order to conceptualise and characterise groundwater recharge in a coastal groundwater system (Figure 1.1). To achieve the main aim of the study three objectives were considered. The first objective focused on measuring the concentrations of environmental isotopes in ground, surface and rainwater. The study considered oxygen-18, deuterium, tritium and carbon-14 due its attractiveness as a multi-faceted approach to constrain groundwater flow paths, evaporative history, ground and surface water interaction, delineate recharge zones and groundwater residence times. The second objective of the study focused on estimating groundwater recharge for the unconfined aquifer using the CMB technique. The hydrochemical approach was chosen to assess the applicability of the method in coastal groundwater system. This chemical approach will provide a good comparison to the results achieved by previous chemical, physical and modelling based methods (Eilers, 2018; Weaver and Talma, 2005; Conrad *et al*, 2004; Timmerman, 1985b; Vandoolaeghe, 1982). The third objective of the study focused on the design of a hydrogeological conceptual model to describe groundwater recharge system using recharge estimates (quantitative) and environmental isotope (qualitative) data obtained from previous objectives. The conceptual model will be used provide understanding of groundwater recharge mechanism for the WCAS and provide insight into interaction between confined and unconfined aquifers and establish sources of recharge to groundwater.

1.8 Scope and outline of the thesis

In chapter 1 a general introduction to the research will be addressed, aim of the study and how the aim will be achieved. Chapter 2 provides a review of key literature relevant to research topic and guides which methods are applicable to achieve objectives. Chapter 3 provides a detailed description of the study area. Chapter 4 discusses methodology and materials used to produce results. Chapter 5 illustrates and discusses the results of objective 1. Chapter 6 illustrates and discusses the results of objective 2. Chapter 7 illustrates states and discusses the results of objective 3 and provides a conclusion on key findings and recommendations.

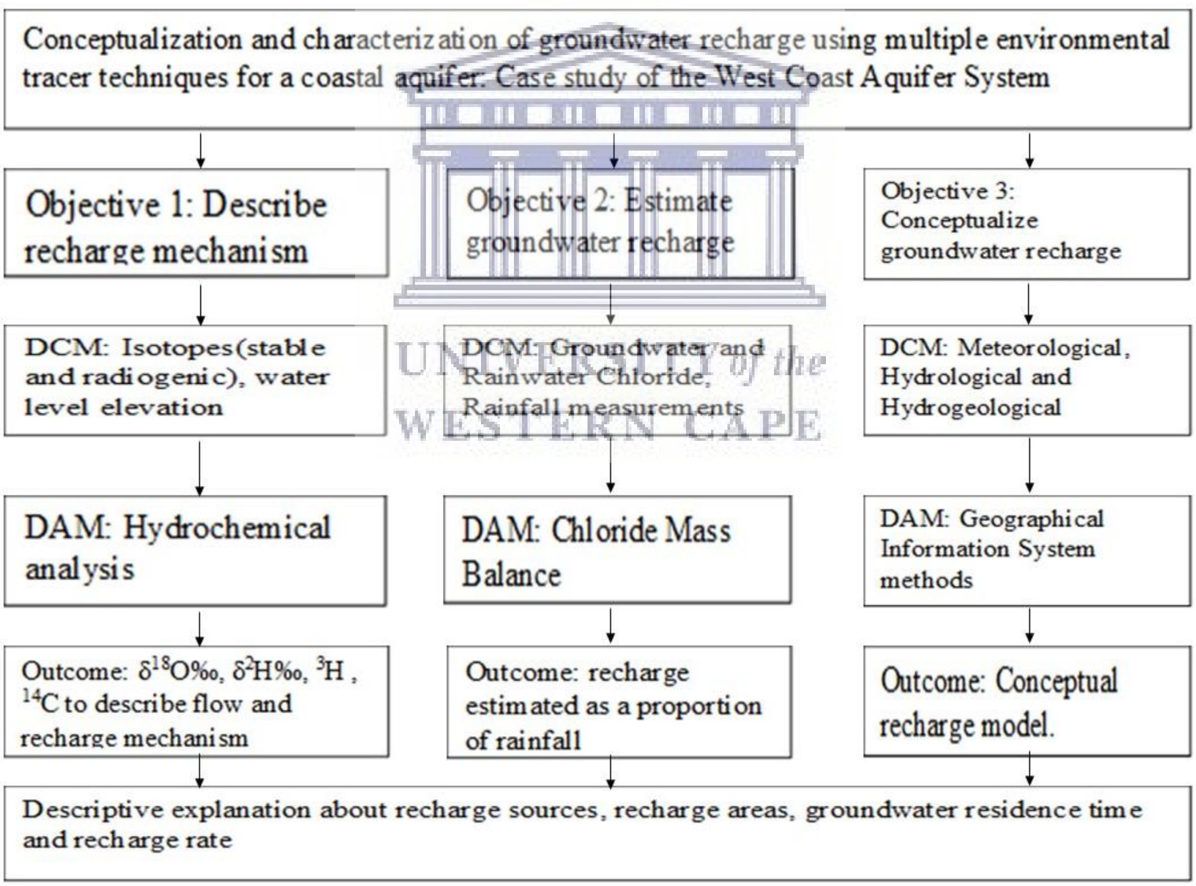


Figure 1: Research framework for the current (Authors Construct)

Chapter 2: Literature review

2.1 Introduction

In order to understand recharge mechanism, it is necessary to do a comprehensive review of available literature. This chapter aims to provide a definition of groundwater recharge, a generic description of the recharge process, physical laws that control recharge, methodologies that can be used to estimate recharge, and methods (e.g. using multiple isotopes) used to establish sources of recharge to an aquifer, and determine groundwater flow and mixing of groundwater. This chapter will also provide a detailed discussion of methods used in this study as the theoretical framework informs methodology for generating and analysing data for the study.This chapter aims to highlight the current regional conceptual understanding of how recharge occurs and the mechanisms that influence recharge, and to ensure that the study being undertaken contributes to a body of work that has not been done within the study area before.

2.2 Occurrence and flow of groundwater

The hydrological cycle describes the continuous movement of water above, on and below the surface of the Earth (Winter *et al*, 1998). The evaporation of water from the ocean and rivers creates moist air that rises. As this air cools, water vapour condenses to form clouds. Global air circulation patterns transport clouds where water then falls to the land surface in the form of precipitation. Once the water reaches the land surface it can either evaporate back into the atmosphere or penetrate the earth surface. Not all water that falls to the land surface is infiltrated by soil. Precipitation can be intercepted by vegetation, form surface runoff as it falls from slopes, through soil as subsurface flow or discharge as surface runoff (Todd and Mays, 2005). Precipitation enters the land surface it becomes soil water, which moves vertically in a downward direction due to gravity or vertically upward due to capillary forces. Soil water percolates until it reaches a depth where fractures and pore spaces are saturated with water, where is then known as groundwater (Freeze and Cherry, 1979). Movement of water in the atmosphere and on the land surface is relatively easy to visualize, but the movement of ground water is not.

A groundwater system consists of an aquifer and aquitard which form the three-dimensional geological deposits which serves as a conduit through which flow takes place (Freeze & Cherry, 1979).Groundwater flow processes is an important is an important part of the hydrological cycle. Groundwater flows through a system made up of pores and fractures, controlled by hydraulic factors such as porosity and hydraulic conductivity. The system of pores and fractures form flow paths of varying lengths that allows inflow of groundwater at recharge areas and flows to discharge areas (Winter et al, 1998). The nature of the water-bearing properties of the geologic formation depends to a large extent on the mineral composition and structure of the formation and the geologic processes that initially formed and then further modified it.

2.3 Groundwater Movement

Movement of groundwater is a continuous process, which occurs at different timescales. Groundwater moves vertically through gravitational forces and horizontally due to hydraulic gradient (Freeze and Cherry, 1979). Hydraulic head is the main factor influencing groundwater flow as the groundwater moves from high water level to low water level. The groundwater level response at a given point in an aquifer depends on the distance of that point from the recharge area and the rate at which groundwater flows through the landscape, which is dependent on aquifer parameters such as transmissivity, hydraulic conductivity and storativity (Kirchner, 2003).

Groundwater flow systems are defined by the boundary conditions imposed by the topography, geology and distribution of recharge (Winter, 1998). Groundwater flow system was first described by Tóth (1962) and discussed detail by Freeze and Witherspoon (1967), Freeze and Cherry (1979), Winter (1998), Winter (1999), and can be divided conceptually into 'local' groundwater flow and regional flow. Flow systems of different sizes and depths can be present which overlie each other and is illustrated by figure 2. The only immutable law is that high lying area are recharge areas and low-lying areas are discharge areas (Freeze and Cherry, 1979).

Local groundwater flow is where water recharge at a water table high and discharge into adjacent lowland (Winter, 1998). Local groundwater systems are the most dynamic and the shallowest flow system. Therefore, these flow systems have greatest interaction with surface water and atmosphere. According to Tóth (1962) that as depth to lateral extent of the groundwater system becomes smaller than the local groundwater systems are more likely to reach the create small series of independent flow cells. Local flow is confined within a single basin enclosed by topographic high points and undulates to relatively shallow depths in the subsurface (James et al, 2000). Groundwater in a local flow system generally has flow paths that are short residence times. According to James et al (2000) environmental isotopes of oxygen and hydrogen can be used to constrain groundwater flow due to direct contact with the atmosphere and the hydrological cycle.

Regional groundwater flow systems are much deeper compared to local flow systems and groundwater primarily travels through bedrock have larger flow paths. Regional groundwater flow paths develop where local relief is negligible and regional relief is significant (Freeze and Cherry, 1979). This groundwater has a longer contact with substrate matrix and generally have longer residence times of thousands of years (Winter, 1998). Regional flow circulates to greater depths and is not necessarily confined within a single hydrological basin (James et al, 2000).

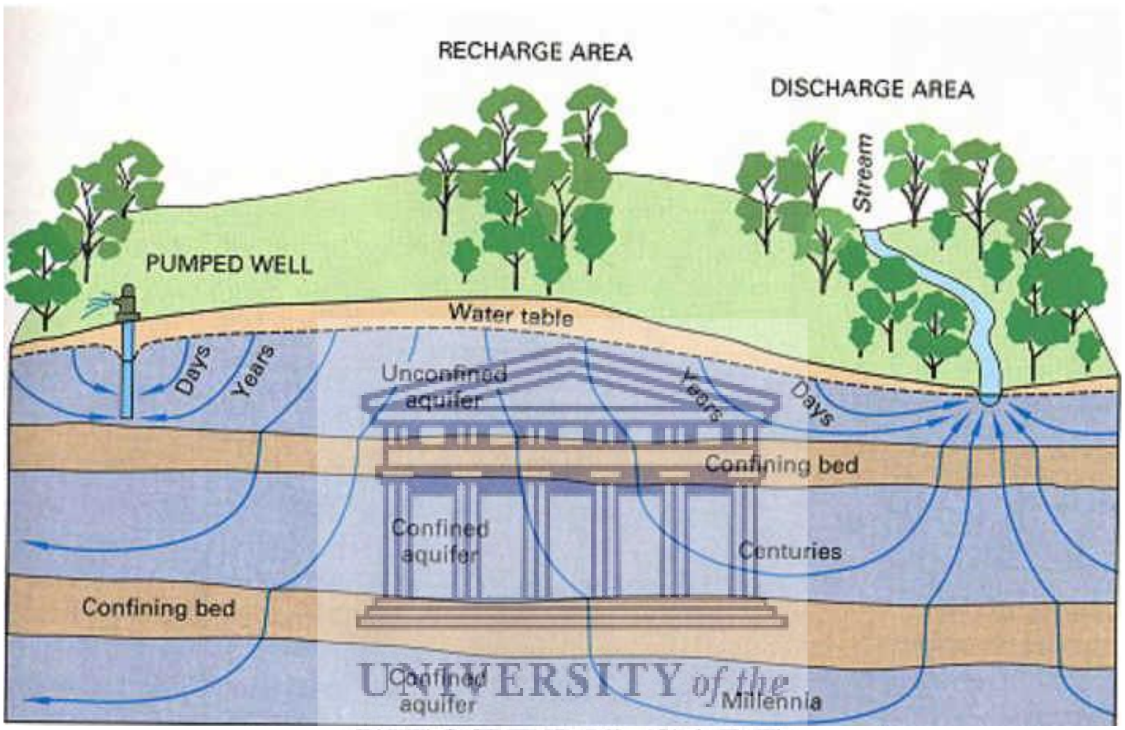


Figure 2: Illustrates groundwater flow paths varying in depth, length and travel times (Winter *et al*, 1998)

2.4 Groundwater-surface water interaction

A conceptual model of recharge processes needs to consider the surface and groundwater flow systems and to what are these entities linked (Healy, 2010). Groundwater-surface interactions provide an important qualitative understanding of groundwater flow system for any recharge investigation (Winter et al, 1998). Winter et al (1998) and Lerner (2003) describes the interaction based on the stream water level in relation to the hydraulic head in the aquifer system which is in hydraulic connection which controls recharge from streams to groundwater and discharge from groundwater to streams. Flow regimes, streambed geology and climate influence the type of groundwater-surface interaction (Healy, 2010; Lerner, 2003; Winter *et al*, 1998). Flow regimes in channels can be classified as perennial, season and ephemeral. Figure 3 schematically represents the types of groundwater-surface water interaction which occur, namely: gaining stream, losing stream.

2.4.1 Types of surface-groundwater interaction

A gaining stream (figure 3 A) occurs where groundwater discharges into a stream channel. For this process to occur the piezometric surface in the vicinity of the stream is always higher than the stream stage. According to Lerner (2003), groundwater in this instance always reaches the stream as the stream and the piezometric surface is always connected. According to Winter et al (1998), the geology of the streambed is usually porous and fractured. The flow regime is generally perennial in the channel. A gaining stream is generally located in lower catchments and provides a discharge route for a groundwater system (Lerner, 2003). Groundwater discharge to streams generally occurs throughout the year, provided that the piezometric surface remains above stream stage.

In a losing stream (figure 3 B) surface water seeps to groundwater. The process occurs when the stream stage is higher than the piezometric surface in the vicinity of the stream. This generally occurs when the flow regime is seasonal. Lerner (2003) classifies these rivers as intermittent streams as the type of interaction alternates seasonally between losing and gaining stream behaviour due to season fluctuations of the piezometric surface and stream stage. The geology of the streambed is usually underlain by alluvial deposits or weathered rock. Losing streams can be connected to the groundwater system by a continuous saturated zone (Winter et al, 1998).

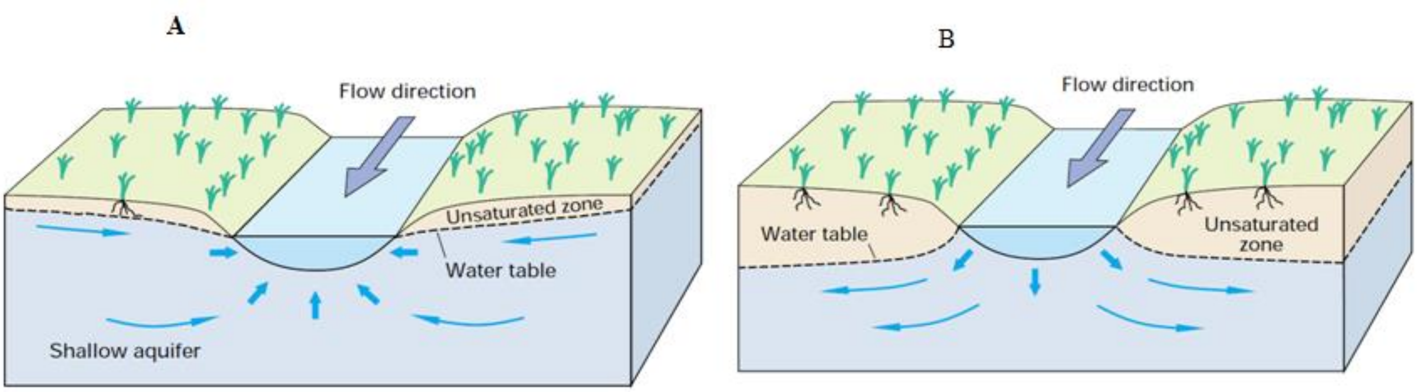


Figure 3: Classification of types of groundwater-surface water interactions: (A) gaining stream,(B) losing stream.

2.5 Definition and mechanisms of natural recharge

Recharge is defined as the downward flow of water reaching the water table subsequently adding to groundwater storage (Healy & Scanlon, 2010; Scanlon, 2003; Simmers, 1992; Freeze & Cherry, 1979). All types of groundwater recharge occur in semi-arid regions. Xu & Beekman (2003) have characterized these types of groundwater movement into modes of recharge. The four modes of recharge are as follows:

1. Downward flow of water through the unsaturated zone reaching the water table;
2. Lateral and/or vertical inter-aquifer flow;
3. Induced recharge from nearby surface water bodies resulting from groundwater abstraction; and
4. Artificial recharge such as from borehole injection or man-made infiltration ponds.

Recharge occurs through diffuse and focused mechanisms (Healy, 2010). Diffuse recharge is distributed over large areas in response to precipitation infiltrating the soil surface and percolating to the water table. Focused recharge is movement of water from surface water bodies or concentrated recharge from small depressions, joints or cracks. The addition of water to a groundwater reservoir does not occur from a single rainfall event. Water level fluctuations can be caused by a series of rainfall events. The time scale and the recharge mechanism depend on the several factors such as the duration of rainfall events, vegetation, land use, irrigation, antecedent moisture of soil, topography depth of the water table, geology and aquifer properties

There are three types of groundwater recharge which are controlled by the hydrological cycle and geology at specific location. According to Xu and Beekman (2003), the three origins of groundwater can be classified as direct, indirect and local recharge (Figure 4). Direct or diffuse recharge is the direct infiltration or percolation through the unsaturated zone to groundwater. Indirect recharge is percolation to the water table through riverbeds. Localized recharge is the accumulation of precipitation in surface water and subsequently concentrated infiltration and percolation through the unsaturated zone to groundwater. Movement of water to the aquifer can occur through piston-type flow or preferential flow mechanisms (Xu & Beekman, 2003). Piston-type flow occurs when precipitation is stored in the unsaturated zone and is displaced downwards by subsequent infiltration. This may also occur without the disturbance of moisture distribution.

Movement of water to the aquifer can occur through piston-type flow or preferential flow mechanisms (Xu & Beekman, 2003). Piston-type flow occurs when precipitation is stored in the unsaturated zone and is displaced downwards by subsequent infiltration. This may also occur without the disturbance of moisture distribution. Preferential flow is the movement of water through preferred pathways, macropores, cracks and fractures of the unsaturated zone with a relatively high infiltration or percolation capacity. Recharge can also occur as point recharge. Point recharge is a site of recharge with no areal extent. Line recharge occurs from a drainage feature such as river or areal recharge in an area of a certain extent.

The present focuses on the first 3 modes of recharge where recharge is a portion of rainfall percolating through the unsaturated zone, recharge as lateral and vertical flow between the upper and lower aquifer units and recharge induced from the nearby Berg River due to differences in hydraulic head and stream stage. Induced recharge (also known as artificial recharge) as a mode of recharge will not be considered in this study. This study focuses on the conceptualization of natural recharge. Groundwater is recharged naturally from earth's hydrological processes such as precipitation, rivers, lakes as well as irrigation and runoff from urbanized areas (Lerner, 1990). For the purpose of achieving objective 2, groundwater recharge will be defined as the portion of rainfall which forms actual recharge and adds to groundwater storage, irrespective of local, direct or indirect mechanisms.

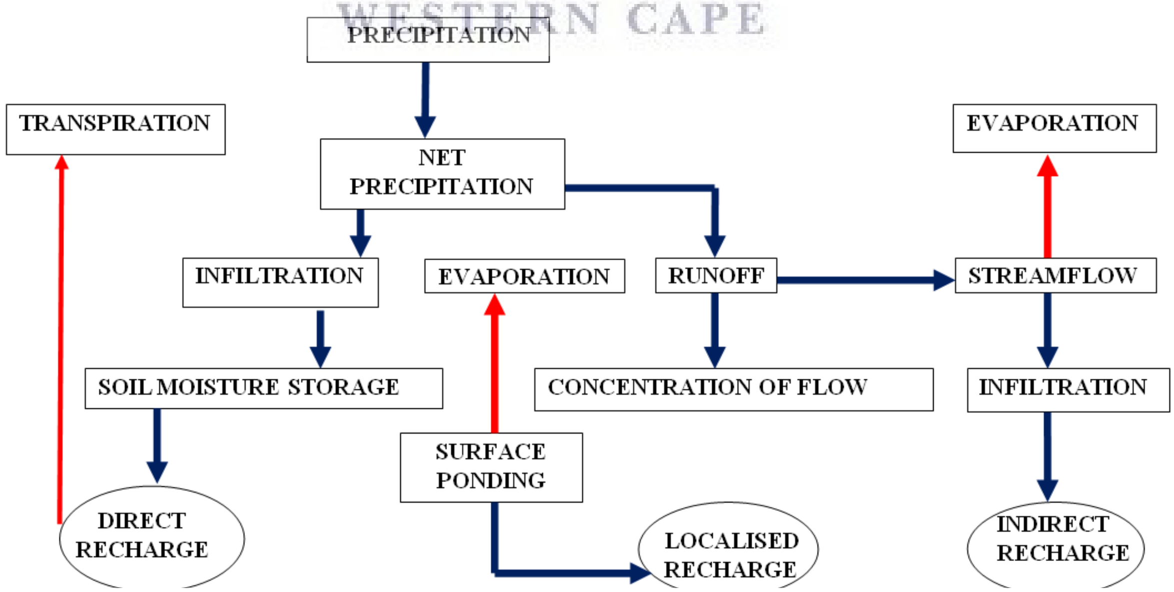


Figure 4: Various elements of recharge in semi-arid region (modified from Lloyd, 1986)

2.6 Factors which control natural recharge mechanism in the semi-arid regions

A conceptual model of recharge mechanism bears importance on the factors that influence recharge. Healy (2010) and Scanlon *et al* (2002) determined the main factors that influence recharge: climate, geology, topography, hydrology, vegetation and land use. These factors are required for the development of a conceptual model. The spatial and temporal variability of climate controls the availability of water at the land surface.

2.6.1 Climate

Climate variability is often the most important factor that controls recharge as precipitation is the source of natural recharge. Recharge is more favourable when precipitation rates exceed evapotranspiration rates. In semi-arid regions evapotranspiration rates are increased in the summer months than in winter rainfall months. Conversely, areas that experience a Mediterranean climate have higher rainfall rates in winter months than summer months. Therefore, the inter-annual variability in climate limits the time that recharge can occur throughout the year. Duration and intensity of individual rainfall events have a significant impact on recharge. In arid regions, focused recharge from ephemeral streams is often the dominant recharge mechanism. Pool (2005) displays that where perennial rivers exist in arid regions such as the creeks in Arizona, inter-annual variability in recharge is dominated by El Nino conditions that produce higher rainfall than in subsequent years where La Nina conditions dominate.

2.6.2 Geology and Soil

Permeability of surface and subsurface material greatly affects natural recharge (Healy, 2010). Sediment arrangement influences movement of water both vertically and horizontally. Water movement is promoted by coarse grained high permeability whereas fine grained low permeability limits the transmission of water. The amount of water moving through a column of coarse-grained soil reaches the water table faster than the same amount of water moving through a column of fine-grained soil. Thus, in areas of fine-grained sediment it is expected that decreased infiltration, enhanced runoff, increased transpiration by vegetation in the unsaturated zone, greater storage and decreased recharge occurs than in areas where coarse grained material dominates the land surface. Permeability is an important factor that controls recharge mechanism in semi-arid regions. Focused recharge in semi-arid regions occurs through porous coarse-grained streambed facilitates movement of water between surface and groundwater water.

2.6.3 Surface Topography

Land surface topography plays an important role in controlling recharge mechanism (Healy, 2010). Steep slopes tend to have low infiltration rates and are prone to facilitate runoff from slopes. Flat land surfaces do not drain water well, therefore favouring diffuse recharge mechanism. Dunner *et al* (1991) observed that even when uniform surface characteristic infiltration at the land surfaces increases down slope a long hill because down slope portions of the hill are more exposed to runoff from upslope portions as well as precipitation.

2.6.4 Vegetation

Vegetation can have a profound effect on recharge in semi-arid regions (Healy, 2010). A vegetated land surface typically has a higher rate of evapotranspiration than an unvegetated land surface, thus decreasing the water available for recharge. Plant root systems are responsible for the uptake of water from the vadose zone. The depth of these root systems influences the ability of plants to extract water from the subsurface. Trees have extensive root systems that can extract water from depths of several meters which plants with shallow root systems cannot reach. Therefore, recharge mechanism is promoted in areas with shallow root systems than in areas with perennial deep rooted vegetation. In most settings, the control of vegetation is seasonal and is related to influences of climate on the lifespan of most vegetation. The natural deterioration of vegetation is termed senescence, which causes plants to wilt and die above the surface and their root systems to contract and shrink in the subsurface. Where root systems are now absent, preferential flow paths are formed which facilitate movement of water, enhance infiltration and subsequent recharge. The distribution and the type of vegetation play an important role in abstraction of water. For example, coniferous forests consume more water while shrubs and grasslands use less water.

2.6.5 Land Use

Land use, and more specifically change in land use, can have profound impacts on groundwater storage. The transition from vegetated land surface to an industrial land surface can significantly alter recharge mechanism and hydraulic regime. Urbanization provides impervious surfaces that reduce diffuse recharge mechanism and increase runoff. This is usually diverted to surface water bodies and increased localized recharge mechanism. Man-made infrastructure created to transport water such as underground pipes and sewers are prone to structural faults which result in leakage. Leaky pipes can form potential recharge that may lead to actual recharge if the infrastructure is not fixed. Irrigated agricultural areas contribute significantly to recharge through irrigation return flow. Irrigation return flow is any excess irrigation water that infiltrates soil beneath the root zone (Healy, 2010). The excess water contributes to recharge. This phenomenon occurs more particularly in semi-arid regions where precipitation rates are low. In Australia, deep rooted Eucalyptus trees were replaced by shallow-rooted crops. The change in the land use resulted in an increase of natural recharge (Scanlon *et al*, 2002). In Niger, the conversion of natural savannah to non-irrigated mullet crops resulted in increased runoff and focused recharge beneath ephemeral streams that are points for discharge.

2.7 Methods to estimate recharge

There are many review articles and publications that explicitly describe recharge estimation (Healy, 2010; Scanlon *et al*, 2002; Xu & Beekman, 2002; Simmers *et al*, 1998; Lerner *et al* 1990). Determination of groundwater recharge in arid and semi-arid areas is neither straightforward nor easy. This is a consequence of the time variability of precipitation in arid and semi-arid climates, and spatial variability in soil characteristics, topography, vegetation and land use (Lerner *et al.*, 1990). Moreover, recharge amounts are normally small in comparison with the resolution of the investigation methods. The greater the aridity of the climate, the smaller and potentially more variable is the recharge flux (Allison *et al.*, 1994).

Humid and semi-arid systems represent end markers for different climates and generally require different approaches to quantify recharge. Scanlon *et al* (2002) provides a review of methods to be applied in different climatic regions, whereas Xu & Beekman focused on methods that are suitable for recharge estimation in generally semi-arid Southern Africa. Recharge rates are limited in large part by the availability of water at the land surface. In turn, this controls the appropriate techniques which are applicable for recharge estimation. Therefore, the selection and application of recharge estimation methods depend on the location of the study area and availability of data to develop such an appropriate recharge conceptual model (Petersen, 2012).

There are three types of estimation, namely: physical, chemical and modelling methods. Physical methods attempt to estimate recharge from water balances calculated either from hydro-meteoric measurements or direct estimates of soil water fluxes based on soil physics or Chemical methods based on the distribution of natural tracers found in rainfall (commonly ^{2}H, ^{3}H, ^{14}C, $^{18}0$ and Cl) in the saturated and unsaturated zone. According to Scanlon *et al* (2002), methods are based upon hydrological zones such a surface water, unsaturated zone and saturated zones. Methods based on unsaturated zone provide estimates of potential recharge which are based upon drainage rates below the root zone. Techniques based on saturated zone studies are applied most commonly over much larger areas. Recharge methods which apply data from the saturated zone provide evidence of actual recharge because water reaches the water table. Some saturated methods include Water Table Fluctuation Method, Darcian Methods, Tracer Techniques, Environmental Tracers and Numerical Modelling.

Various factors need to be considered when choosing a method to quantify recharge. Scanlon *et al* (2002) states that purpose of the recharge must include spatiotemporal scale, as this dictates the appropriate technique required to achieve objectives of the study. According to Scanlon *et al* (2002), the first step is to define the groundwater system in terms of the geological structures and the resultant flow mechanisms. Second, the complete water balance must account for all water that 'does not become recharge' and the underlying groundwater recharge processes clear. Third, the estimate must consider the time scale for the recharge process.

Xu & Beekman (2002) provide a review of recharge estimation in semi-arid Southern Africa. The literature reviewed the following methods as the most promising in semi-arid regions:

- Cumulative Rainfall Departure
- Water Balance Method
- Chloride Mass Balance
- Water Table Fluctuation
- Saturated Volume Fluctuation
- EARTH Model

2.7.1 Physical Methods

Physical methods are based on the direct measurement of hydrological parameters and used to estimate diffuse recharge mechanism. The greatest advantage is that these techniques are quick, inexpensive and straightforward. However, physical methods are often problematic in semi-arid regions. Scanlon *et al* (2002) notes that the major limitation in semi-arid and arid regions is the generally thick unsaturated zone and low rainfall rates. The combinations of these factors make it increasingly difficult to measure such small changes in hydrological parameters directly. An example of such method would be the Darcy's Law Method.

Darcy's Law Method

Darcy's law is used to calculate recharge for flow in the unsaturated and saturated zone and has been used widely for recharge investigations is given in Equation 1 (Healy, 2010).

$$R = -\mathrm{K}(\theta)\left(\frac{\mathrm{d}h}{\mathrm{d}z} + 1\right) \qquad \text{Equation 1}$$

Where: K (θ) = the hydraulic conductivity at the ambient water content θ (m/d) h = the matrix pressure head (m) z = elevation (m)

A major advantage of using this method is that it is not limited to certain times of the year. The method has been applied to semi-arid regions and it allows for monitoring of individual events, therefore providing insight into the mechanics of recharge (Healy, 2010). Major limitations associated with this method include the highly variable nature of hydraulic conductivity and the limited accuracy with which unsaturated hydraulic curves and gradients can be measured.

Water Balance Methods

The Water Balance Method is commonly used for estimating recharge (Healy, 2010; Scanlon *et al*, 2002). Water Balance Methods can be applied over a wide range of time and space scales encountered in hydrogeological studies. The major limitation of water balance method is the accuracy of recharge estimate is dependant in the accuracy with which individual components in the water balance can be determined. This limitation is important in semi-arid regions when the magnitude of recharge is significantly smaller relative to measured variables, which may lead to result in large uncertainties in recharge estimation. The advantages of using water budget methods are that they are generally not bound by assumptions of mechanisms of water movement to an aquifer. A simple water budget analysis used in many hydrological studies is based on a soil column that extends downward land surface to some depth. The principle is that other environmental factors such as precipitation and evaporation can be measured more easily than recharge. The hydrological water balance for an area can be defined as in Equation 2:

$$R(t) = P(t) - E(t) - Q(t) - \Delta\theta(\mathrm{t}) \qquad \text{Equation 2}$$

Where R(t) is recharge, P(t) is precipitation, E(t) is evapotranspiration, Q(t) is runoff, and Δ(t) is change in volumetric water content. The term (t) designates that the terms are distributed through time (Sun, 2005).

2.7.2 Chemical methods

Environmental tracers have a wide variety of uses in hydrogeological studies, providing qualitative and quantitative estimates of recharge. Environmental tracers include ions, isotopes or gases which are soluble in water and can be detected in the atmosphere, surface water and the subsurface (Healy, 2010). Such environmental tracers include Carbon 14, Tritium, Deuterium, Oxygen-18 and Chloride. These tracers can provide insight into the entire hydrogeological system such as identifying sources of recharge, information on velocities of flow and residence times of groundwater and estimating recharge (Clarke & Fritz, 1997; Healy, 2010; Scanlon *et al*, 2002; Xu & Beekman, 2002; Simmers et al, 1998; Lerner *et al* 1990). Lerner *et al (*1990) and Healy (2010) separates chemical tracer techniques into signature methods and throughput methods. Applied tracers are normally only used in qualitative methods which track and date water in the subsurface, Carbon 14, Tritium, Deuterium, Oxygen-18 are examples of applied tracers. Throughput methods are based on the principle of the conservation of mass which compares the concentration of tracers in precipitations against that of groundwater. Chloride is probably the most commonly used tracer for throughput method due to its conservative nature. The method is based on the principle that hydrochemically stable major ion chloride is solely derived from precipitation. The main limitation of the method is that all environmental tracers do not measure water movement directly, which may lead to an over or under- estimation of recharge. According to Sun (2005), the main problems associated with environmental tracers are unknown tracer inputs in the subsurface, mixing and dual flow mechanisms.

Chloride Mass Balance Method

The groundwater chloride mass balance method is the most commonly used environmental tracer method used for recharge estimation. A method to estimate recharge exists for the unsaturated (Equation 3) and the saturated zone (Equation 4). In the equation to estimate recharge in saturated zone drainage is replaced by recharge and chloride in the unsaturated zone is replaced chloride concentration in groundwater.

$$\frac{d(S_u \cdot c_u)}{dt} = F \cdot c_s - R \cdot c_u - T_u \cdot c_t \qquad \text{Equation 3}$$

$$\frac{d(S_g \cdot c_g)}{dt} = R \cdot c_u + Q_{lgi} \cdot c_{gi} \cdot c_{gi} - T_g \cdot c_t - Q_g \cdot c_g - Q_{lgo} \cdot c_g \qquad \text{Equation 4}$$

The advantage of using the saturated zone equation is that unlike the unsaturated zone method, the saturated method is not sensitive to mechanisms of flow. This advantage ensures that all chloride in the saturated zone is accounted for irrespective of the mechanism preferential flow. A limitation of the unsaturated zone method is that it requires sensitive data acquisition, making it an advantage for data collection using the saturated zone method as water samples are easier to collect. Johnson (1987) conducted a recharge investigation where the estimated recharge rate from the unsaturated and saturated methods was compared. The outcome of the study was that the unsaturated zone had a recharge rate that was twofold higher than recharge rates estimated with the saturated zone method. The higher recharge rate using the saturated method was due to higher chloride concentration due to preferential flow as well as method used for extracting water from soil using usually dilutes the chloride concentration, which subsequently leads to under-estimation of recharge rate.

The use of natural environmental tracers such as chloride has been used as a tracer due to its conservative nature. Its conservative nature stems from its anionic form as it does not absorb onto negatively charged silicates. Therefore chloride does not participate in any geochemical or biochemical reactions. The Chloride Mass Balance has been applied in different climates and is overall one of the most popular methods for recharge estimation. Use of chloride mass balance method is one of the few techniques that can estimate very low recharge rates and is generally the most accurate in this regard (Scanlon *et al*, 2002). The profile of chloride in the soil profile varies with different land cover types (Healy,2010; Shimelis, 2012).In pristine areas where natural vegetation dominates, the concentration of chloride typically forms a bulge in the root zone or near the surface. In unvegetated areas the chloride bulge is displaced downwards from the root profile entirely.

Analytical uncertainties in chloride measurements and uncertainties in chloride inputs restrict the upper range of recharge rates that can be estimated with the CMB technique. Saturated zone studies spatially integrate recharge fluxes over large areas (Scanlon *et al*, 2002). Using tracers to date groundwater near groundwater divides may provide estimation of local recharge rates. Because of the uncertainties associated with each approach for estimating recharge, the use of many different approaches in recommended to constrain the recharge estimation (Scanlon *et al*, 2002). In many cases different approaches complement each other and refine the conceptual model of recharge processes (Healy,2010).

Table 1: Recharge estimation methods applied in semi-arid Southern Africa (Xu and Beekman, 2003)

Zone	Approach	Method	Principle	Reliable	Ease	Cost
Surface Water	Physical	HS	Stream hydrograph separation: outflow, evapotranspiration and abstraction balances recharge	Med-high	Low	Low
		CWB	Recharge derived from difference in flow upstream and downstream accounting for evapotranspiration, in and outflow and channel storage change	Med-high	Med	High
		WM	Numerical rainfall-runoff modeling; recharge estimated as a residual term	Med	Med-high	High
Unsaturated	Physical	Lysimeter	Drainage proportional to moisture flux / recharge	Med	High	High
		UFM	Numerical rainfall-runoff modeling; recharge numerical solutions to Richards equation	High	Med	Med
		ZFP	Soil moisture storage changes below ZFP (zero vertical hydraulic gradient) proportional To moisture flux / recharge	High	Med	Med
	Tracer	CMB	Chloride mass balance: Profiling drainage inversely proportional to Cl in pore water	Med	Low	Low
		Historical	Vertical distribution of tracer as a result of activities in the past	Med-high	Med-high	High
Saturated-Unsat	Physical	CRD	Water level response from recharge proportional to cumulative rainfall departure	Low-Med	Low-Med	Med

Zone	Approach	Method	Principle	Reliable	Ease	Cost
		EARTH	Lumped distributed model simulating water level fluctuations by coupling climatic, soil moisture and groundwater level data	Low-Med	Med	Low
		WTF	Water level response proportional to recharge /discharge	Med	Low	Low
	Tracer	CMB	Amount of Cl into the system balanced by amount of Cl out of the system for negligible surface runoff / runoff	Med	Low	Low
Saturated	Physical	GM	Recharge inversely derived from numerical modeling groundwater flow and calibrating on hydraulic heads / groundwater ages	Med-Low	High	High
		SVF	Water balance over time based on averaged groundwater levels from monitoring boreholes	Med-Low	Med-Low	Med
		EV-SF	Water balance at catchment scale	Med-Low	Med-Low	Med-Low
	Tracer	GD	Age gradient derived from tracers	High	Med	High

Abbreviations			
HS	Hydrograph Separation- Baseflow	CRD	Cumulative Rainfall Departure
CWB	Channel Water Budget	WTF	Water Table Fluctuation
WM	Watershed Modeling	GM	Groundwater Modelling
UFM	Unsaturated flow modeling	SVF	Saturated Volume Fluctuation
ZFP	Zero Flux Plain	EV-SF	Equal Volume- Spring flow
CMB	Chloride Mass Balance	GD	Groundwater Dating

2.8 Global context on groundwater recharge in the semi-arid environment

Grismer *et al* (1999) investigated natural recharge in semi-arid coastal region with relatively complex geology in California, United States of America. The study focused on using the most commonly used field methods to estimate natural recharge in non-irrigated and irrigated orchards.

The CMB, Soil Moisture Balance (SWB) and soil-moisture monitoring (NP) were methods selected for the study. The CMB overestimated natural recharge in relation to other methods for no- irrigated orchards. In irrigated orchards the chemical mass balance provides recharge estimates that were similar to SWB and NP. The study also recommends that when using CMB Method, it is important to use other methods to validate recharge estimates. Of the three methods, CMB was found to be the simplest, least encumbered and provide a long-term assessment of natural recharge than the other methods used.

Gaye & Edmunds (1995) investigated natural recharge in north-western coast of Senegal. The study used CMB and tritium to estimate recharge in the region. Using CMB Method, recharge was estimated at 10% of the average precipitation 290 mm/annum that the region experiences. Recharge estimation using CMB was investigated for the unconfined aquifer. A conceptual model was not developed to describe the natural recharge system in the area. Chloride concentration was measured from a moist 50mg soil sample. The investigation revealed that when comparing recharge estimates for both tritium and chloride, both environmental tracers are good indicators of water movement in unsaturated porous media. Gaye & Edmunds conclude the investigation stating that the CMB represents the most widely applicable and most reliable technique for recharge estimation in unconsolidated media in semiarid regions, regardless whether the method is applied in coastal regions or further inland.

2.9 Local context on groundwater recharge in the semi-arid environment

In 1974 the first hydrogeological investigation was undertaken in the West Coast to explore potential groundwater supply close to the Langebaan Lagoon. In 1985, Timmerman reported on the natural recharge mechanisms and the exploitation potential of water in the Lower Berg River Catchment. Timmerman has delineated the Northern regions as high recharge area, as rainfall is higher in the southern region (Grootwater) and decreases north to the Adamboerskraal aquifer. Timmerman also highlighted the high-lying area between Langebaan and Hopefield as areas that will favored as a recharge zone. The study provided at the time a comprehensive hydrogeological only for the primary aquifer and neglected to provide the same hydrogeological information for the confined aquifer units. Timmerman estimated natural recharge to the four primary aquifer units without using any method but by postulating a recharge estimate based on the calculated hydraulic conductivity data, geological and precipitation data. For the all primary aquifers in the West Coast, direct recharge was estimated at 15% of annual precipitation, based on estimates calculated for the Atlantis Aquifer.

Groundwater recharge estimation has been by numerous investigators in the past. Talma and Weaver calculated natural recharge to the unconfined and confined aquifer of the Langebaan Baan Road Aquifer. The Chloride Mass Balance (CMB) was used to quantify recharge to the unconfined aquifer and confined aquifer. An assumption of CMB is that it should be applied to unconfined aquifers. However, Weaver and Talma (2005) applied this method to confined aquifer unit and estimated the recharge to be 11.5% from rainfall.

Conrad *et al* (2004) estimated natural recharge to a primary aquifer for the West Coast region. A range of methods was used to estimate natural recharge in the coastal region, CMB. Saturated Volume Fluctuation (SVF), Cumulative Rainfall Departure (CRD) Method and Extended model for Aquifer Recharge and soil moisture Transport through the unsaturated Hard rock (EARTH) Method. These are all methods that are found to suitable for recharge estimation in semi-arid environments. The results of the investigation found that previous recharge estimates were overestimated and that direct recharge percentages in the region of 0.2 to 3.4 % are considered to be more realistic (Conrad et al, 2004). When comparing the results of CMB to other methods used, it was found that CMB recharge estimates fall within an expected range and is suitable for use in a coastal environment as other methods are.

Sun *et al* (2013) estimated recharge using Rainfall Infiltration Breakthrough (RIB) Method in 2 study areas; one in a coastal alluvial aquifer (Riverlands) and the other in the Table Mountain Group (TMG) shallow unconfined aquifer (Oudebosch). The RIB Method was selected as the investigators interpreted the CMB Method to be inadequate in providing accurate recharge estimate in South Africa. The findings of the recharge estimates using the RIB model conclude that the method is best suited for shallow unconfined aquifers with relatively lower transmissivity. The study recommended that the utility of the RIB model for application in different climatic areas under different hydrogeological conditions needs to be further explored.

Du Toit & Weaver (1995) conducted a groundwater investigation at the Saldanha Steel Plant, about 10 km north of Saldanha. They calculated a recharge of 8% from water level data from boreholes on the adjacent property, Namaqua Sands. At Saldanha Steel, using reverse modeling techniques, they calculated 12% for recharge (Talma and Weaver, 2005).

2.10Environmental Tracers

2.10.1 Introduction

Environmental tracers are defined as ions, isotopes or gases that move with water that can be detected in atmosphere, surface waters and the subsurface (Healy, 2010). Based on the theory of tracing and Darcy, hydrochemical patterns are influenced by groundwater flow. Therefore, this section will focus on the factors controlling environmental tracer activities in groundwater, surface ad rainwater. These factors will be discussed within the context of a coastal hydrogeological environment and the application of environmental tracers in recharge studies. Environmental tracers can be classified as either radioactive or stable. Radioactive or stable tracers can be further which can be considered as either natural or artificial (Healy,2010; Aggarwal,2016). Tracers can be further divided into three categories following the nomenclature by Scanlon *et al* (2002): natural, historical and applied tracers. This study uses natural and historical tracers as they are created within the atmosphere because they water soluble and can be transported and traced throughout the hydrological cycle. Natural tracers are chloride and stable isotopes of the water molecule (Clark & Fritz, 1997). Historical tracers include tritium and carbon-14 that have been introduced into the atmosphere by anthropogenic activity (Healy, 2010). There are many review articles and publications that explicitly describe the role of environmental tracers in hydrological and hydrogeological studies (Craig, 1961; Dansgaard, 1964; Freeze & Cherry, 1979; Clark & Fritz, 1998; Kendall & McDonnell, 1998; Gat, 2001, Healy, 2010).

The distinct advantage environmental tracer methodologies have over artificial tracers is that they facilitate the study of various regional hydrological processes to obtain time and space integrated characteristics of groundwater systems (Aggarwal *et al*,2016). Artificial tracers or applied tracers are generally used for local and site-specific applications. Groundwater recharge occurs at regional flow systems which is why natural environmental tracers will be used in this study. Environmental tracer techniques are effective techniques for fulfilling critical hydrogeological needs such as establishing the origin of groundwater (González-Trinidad, 2017;Satrio, 2017; Keesari, 2017, Craig,1961), the determination of its age (Atkinson,2014) the interlinkages between surface water and groundwater (Kpegli *et al*,2018).

2.11 Review of Stable isotopes ($\delta^{18}O$ and $\delta^{2}H$)

Environmental isotopes of δ^{18}O (oxygen-18) and δ^{2}H (deuterium) are the most frequently used in regional hydrological studies as they integrate small-scale variability to provide an effective indication of catchment-scale processes (González-Trinidad, 2017). According to Käss (1998) this is due to the water vapor pressure of ±2000 $^1H_2\,^{18}O$-molecules and ± 320 $^2H^1H\,^{16}O$-molecules among 10^6 $^1H\,^{16}O$-moecules. The water vapor pressure of the isotopically lighter water ($^1H_2\,^{16}O$) is higher than for isotopically heavier water (^2H and ^{18}O). All phase transitions, also known as fractionation, cause alterations in the isotope content of water. The stable isotopes of light elements show a greater variation because they have greater variations. The variations are due to the energy difference between chemical bonds involving different isotopes of an element due to the differences in relative mass between isotopes (Kendall & McDonnel, 1998; Käss, 1998; Aggarwal, 2016). The value in stable isotope techniques in recharge investigations exist in $\delta^{18}O$ whilst δ^2H are for waters of a different origin (Freeze & Cherry, 1979; Muir & Coplen, 1981).

Stable isotope concentrations of oxygen-18 and deuterium are generally expressed in δ units (Dansgaard, 1964). Isotope ratios are typically reported as per mil (denoted ‰) deviation from a standard as expressed in Equation 5:

$$\delta = \left(\frac{R}{R_0}\right) - 1 \qquad \text{Equation 5}$$

Where 'R_0' is the isotopic ratio of the standard and 'R' is the ratio of the heavy to light isotope sample. A positive delta value means that the isotopic ratio of the sample is higher than that of the standard whilst a negative value means that the ratio of the water sample is lower than that of the standard. A positive value indicates that the sample is enriched in heavy isotopes whereas a negative value indicates that a sample is depleted in heavy isotopes. Craig (1961) suggested that the δ values are reported relative to the Standard Mean Ocean Water (SMOW) or the internationally agreed sample of ocean water named the VSMOW (Vienna-SMOW).

The relationship between hydrogen and oxygen distribution was first proposed by Craig (1961). Since then the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) have made cumulative long-term observations in the 18O and 2H content in rainfall globally (Aggarwal *et al*, 2016) The linear relationship that was established between the stable isotopes of water is called the Global Meteoric Water Line (GMWL). The linear relationship is represented by Equation 6.

$$\delta^2 H = 8 \cdot \delta^{18} O + 10 \qquad \text{Equation 6}$$

The GMWL provides a reference by which differences in the isotopic composition of sampled water in the West Coast can be compared against to interpret effects of temperature and evaporation of water. According to Clark & Fritz (1997) if samples have been subjected to evaporation effects, the ^{18}O and ^{2}H relationship will not plot on the GMWL. According to Gat (2001) this is due to non-equilibrium kinetic effects evaporation of lighter molecules which are preferentially enhanced in the vapor and evaporation. Furthermore, during the condensation of vapor to liquid, heavy isotopes are enhanced. As a consequence, kinetic fractionation water in different stages in the hydrologic cycle develops its unique signature. This study therefore attempts to ratio between light and heavy stable isotopes of water and its unique signature to assess linkages between rainwater, surface and groundwater in order to establish sources of recharge. The stable isotope assessment will contribute qualitative data that will be used as input for the design of the hydrogeological conceptual model.

Variations in the stable isotope content in precipitation and subsequently groundwater as a consequence recharge are consequences of fractionation in hydrological cycle .Craig(1961) have identified several key factors that control the actual stable isotopic composition of precipitation that water that reaches the ground. It is fundamental to identify which effects have the greatest influence on precipitation isotopic composition in coastal environments such as the West Coast. When rainfall measurements are lower than the long-term average these effects could lead to individual rainfall events that have significant impression on a hydrological system (Laar, 2018). These effects allow the use of these isotopes to delineate various recharge processes (Aggarwal *et al*, 2016).

1: Latitude effect: The composition of $\delta^{18}O$ and $\delta^{2}H$ in rainwater generally is more depleted at heavy isotopes at higher latitudes than at low latitudes. Condensation and rainout favours more negative δ values in mid-latitudes such as the South Africa where temperatures are cooler. This will result in vapour that is more depleted than vapour that forms near the equator.

2. Continental effect: The composition of δ values in precipitation becomes depleted in heavy isotopes as air mass travels from the coast further inland. Regions which experience winter rainfall with cooler temperatures and cool air masses. Air masses further inland reduce evaporation which subsequently increases equilibrium fractionation factor that applies during the condensation. Increased equilibrium fractionation results in precipitation further inland being negative in δ

values. This effect is likely to have an impact on rainfall systems originating from the Atlantic Ocean along the West Coast.

3. Altitude effect: The δ values of $\delta^{18}O$ and $\delta^{2}H$ becomes more depleted in heavy isotopes as altitude increases. This phenomenon is caused by progressive rainout of heavy isotopes during orographic uplift and decrease in temperature causes the isotopic composition to be depleted in heavy isotopes. Typical change in δ values range from -0.1 to -0.5‰ per 100m increase in elevation (Käss, 1998). This effect is caused by increased rain at the higher elevations due to continuous cooling of the air mass pseudo-adiabatically to below the dew point in an orographic precipitation system (Kendall & McDonnel, 1998).

4. Seasonal effects: Variation of $\delta^{18}O$ and $\delta^{2}H$ in precipitation is related to seasonal variation within a region. The seasonal changes in the δ values are due to seasonal changes in relative humidity, temperature and evaporation. Seasonal fluctuation in isotopic composition are more predominant in the source regions away from the coast whereas in coastal regions seasonal variation is small.

5. Amount effect: Large rainfall events tend to be more depleted in heavy isotopes relative to smaller events. The intensity and the duration of large rainfall events lead to the rainout of heavy isotopes as more vapour and cloud droplets are removed until the air below the cloud becomes saturated and colder. This reduces he evaporation effects individual raindrops.

The above-mentioned effects have major controls on the δ values of local precipitation in regional groundwater recharge studies. Therefore, it is crucial to compare the rainfall stable isotopes composition to the stable isotope composition of other aspects of the hydrological cycle. This change in isotopic composition by the transition of light to heavy isotopes in physical equilibrium can assist with recharge mechanism by identifying sources of recharge and evaporative history of precipitation prior to recharge of groundwater (Kass, 1992).

2.12 Radioactive isotopes

The radioactive environmental isotopes have been employed in hydrogeology include 3H, 14C, 36Cl, 39Ar, 32Si and 85 Kr (Clark & Fritz). According to Kpegli *et al* (2017) 39Ar and 85Kr is restricted to a limited number of research laboratories due to complicated sampling techniques, difficulty in determining half-life or the half-life not in the range for sub-modern carbon interpretation of these isotopes. Furthermore, the assessment of these isotopes requires large volumes of water to be extracted in the field for analysis to be used in low level counters. Radioactive environmental isotopes of ^{14}C and ^{3}H have proved useful and are the most commonly used in groundwater recharge to determine groundwater age (Vogel, 1974; Atkinson, 2017; Keesari, 2017; Kpegli, *et al*, 2017) to constrain groundwater flow paths.

2.12.1 Tritium

Radioactive isotopes of tritium (^{3}H) are produced natural in the atmosphere through cosmic bombardment of ^{14}N with cosmic ray produced neutrons (Clark & Fritz, 1997). Moreover, nuclear weapon testing in 1950-1963 are anthropogenic sources which were added to the natural stores of tritium in the atmosphere (Freeze & Cherry, 1979). The anthropogenic tritium peak pulse in the atmosphere provides a means by which the age of water can be determined (Kendall & McDonnell, 1998). Prior to nuclear bomb testing tritium activities have been determined to be between 5-110T.U, also referred to as background tritium levels (Gat, 2001). Both natural and anthropogenic tritium enter the hydrological through via precipitation. Tritium has been used as a dating tool for modern groundwater due to its half-life of 12.43 years (Clark & Fritz, 1997). For paleo-groundwater ^{14}C should be used as it has a longer half-life of 5730 years. Based on its short half-life, tritium can only be used to date groundwater short residence time of up to 100 years (Vogel, 1974) According to Atkinson(2014) the decay of tritium bomb pulse peak in the southern hemisphere to near background levels unique ages may be determined from single point measurements. Tritium is part of the water molecule and there is negligible change to ^{3}H activities other than decay. Tritium is an excellent tracer in recharge studies as its movement can be traced through the hydrological cycle, its and can be used as evidence of active and actual recharge (Vogel, 1974; Kendall & McDonnell, 1998; Clark & Fritz, 1997; Geyh, 2001; Keesari, 2017).

Tritium was part of the first studies by Dr. Brown in Canada to monitor atmospheric fall from nuclear tests. According to Kendall & McDonnell (1998) tritium concentrations in the atmosphere has been lost to oceans as they are naturally tritium-free due to the long residence time and large volume area of the ocean.

As a result of radioactive decay, groundwater derived from precipitation that fell before the onset of atmospheric testing of nuclear weapons in 1953 would have contained not more than 0.5 TU in 2000 (Dassi, 2010). Therefore, groundwater tritium activities which are greater than pre-bomb concentrations serve as evidence for direct recharge.

Radioactive isotopes are important tools for confirming active recharge and determining residence time in groundwater as a result of their isolation. However, tritium activities in precipitation have been measured as high as 100 T.U in 1960's and have steadily decreased to 2-3 T.U (Talma & Van Wyk, 2003; Swana, 2017). Groundwater today seldom have more than 50T.U and are typically in the range of <10T.U range (Clark & Fritz, 1997).

Tritium is reported in absolute concentrations using tritium units (T.U) or by radioactive decay (Clark & Fritz, 1997). Tritium units do require a reference standard like stable isotopes as oy is an actual ratio and not analogous. Tritium may be reported in terms of activity or decay.

2.12.2 Carbon 14

The discovery of radiocarbon (^{14}C) in the atmospheric CO_2 was by Libby in 1946. This discovery lead to the development of the first model for dating groundwater using radiocarbon was proposed by Münnich in 1957. Since then, several laboratory and theoretical studies as well field measurements have been made to test radiocarbon dating techniques. In nature ^{14}C concentration of various carbon reservoirs on Earth are in steady state although depending on their interaction with atmospheric decay and burial. These steady values can vary between atmospheric concentration (0.226 Bq per gram of C) to virtually zero (Gat, 2001). Like tritium, radiocarbon occurs naturally in the atmosphere due to the bombardment. Atmospheric radiocarbon concentrations are also impacted by anthropogenic contributions. The combustion of fossil fuels and above ground nuclear weapon testing have caused a pronounced spike in radiocarbon testing in 1964, causing disequilibrium in the steady-state conditions(Clark & Fritz, 1997; Gat,2001). Currently fossil fuel consumption is four times higher than what it is was in 1950's. This, coupled by the dilution of ^{14}C in the atmosphere from dead CO_2 and a decrease in the spike ^{14}C caused by nuclear bomb test, has been 'washed out' but can be found in plant material and the ocean.

Dating groundwater with radiocarbon cannot be done on the water itself due to its natural composition but must rely on dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in water (Freeze & Cherry, 1979). Both forms enter the groundwater from atmospheric $^{14}CO_2$ in in the soil zone. Carbon-14 has a half-life of 5730 which makes it an ideal tool for dating groundwater of sub-modern age.

Unlike tritium, ^{14}C activities are referenced to an international standard known as modern carbon (pMC). The activity of modern carbon is defined by 95% of the ^{14}C activity in 1950 of the NBS oxalic acid standard (Clark & Fritz, 1997). This is close to the activity of wood grown in 1890 in a fossil-CO2-free environment. Therefore, measured ^{14}C activities are expresses as a percent modem carbon (pMC)

2.13 D-excess

A strong relationship exists between the isotopic composition of water evaporated from seawater and ambient relative humidity (Dansgaard, 1964). The y intercept of 10‰ in the GMWL is called the deuterium excess or d-excess value for the Craig's GMWL and was first described by Dansgaard in 1964 (Kendall & McDonnell, 1998).Global atmospheric water vapor forms with an average humidity significantly greater than 85% (Clark & Fritz, 1997). At this humidity precipitation is displaced by 10‰ for deuterium which is why Craig's MWL for global precipitation has a deuterium excess of 10‰ (Clark & Fritz, 1997). The global average of the GMWL is 10‰, however some regions have different intercepts due to difference in humidity, wind speed and proximity to the coast (Clark & Fritz, 1997; Kendall & McDonnell, 1998; Mook, 2001).

Measuring differences in molecular compounds can be done by a variety of mass spectrometry techniques which analysis a host of stable environmental isotopes such as $^{18}0$, ^{2}H, ^{13}C, ^{34}S , ^{15}N, $^{3}5Cl$, ^{37}Cl and ^{85}Sr. less commonly applied isotopes in geochemical research include those of strontium, lead, radon, helium, radium, lithium and boron. These isotopes are not used because the ratio of these isotopes is altered by geological and biological materials as water moves through the subsurface (Kendall & McDonnell, 1998; Clark & Fritz, 1997). Furthermore, these isotopes have not been employed in hydrogeological studies as the analysis is expensive, restricted to a limited number of research laboratories or require large volumes of water samples. Reservations should be made when taking large samples in a semi-arid region that is experiencing drought when groundwater system is sensitive to salinization and abstraction should be done sustainability. Therefore, environmental tracers of 18O, 2H, 3H and 14C are applied in this study as they are conservative in nature, the analysis does not require large quantities for analysis and is inexpensive.

Previous hydrogeological studies that apply oxygen-18 and deuterium seldom use the d-excess fail to provide insight into sources of moisture, atmospheric process, movement of air masses and identify recharge areas. According to Kendall & McDonnell (1998) typical d-excess values range from 0-20.Deep groundwater in confined aquifers in arid region are commonly observed to have low d-excess values and expected to plot below the GMWL. Groundwater d-excess in arid basins have been observed to be in the order of 5-6 (Kendall & McDonnell, 1998). Low d-excess values are caused by evaporation and the meteoric water was initially evaporated from the ocean under more humid conditions than the present day. Sami (1992) studies the d-excess values of deep groundwater in the Eastern Cape province of South Africa. The d-excess value of groundwater ranged from ±6 for deep groundwater with an evaporation slope of 5.4. The d-excess value can be attributed to groundwater that had not experienced significant evaporation effects and that groundwater must be replenished by infiltrating water which is not affected by evaporation.

2.14 Previous studies focusing on the application of environmental isotopes in recharge investigations

Laar (2018) used d-excess vales of rainwater and groundwater to understand the evaporative history of groundwater and the contribution of moisture of air mass controls isotope composition of rainfall events. The study was done in a coastal area in Ghana where it was found that a wide range of d-excess in rainwater (-6.0—19.04) was due to the contribution of local isolated air masses resulting in low d excess values. Laar (2018) attributed high d-excess values greater than 10‰ from groundwater samples and hypothesized the existence of a bimodal rainfall system or the addition of kinetically controlled reevaporated which affects the deuterium signature due to the preferential absorption of lighter isotopes. Laar (2018) found that low groundwater d-excess values (<6‰) suggests that there is significant evaporation of rainwater leaving residual groundwater with lower d-excess values. This is indicative climate the study area which is influenced by the Atlantic Ocean with a high and uniform relative humidity. The results obtained from Laar (2018) are important for the present study as it provides an understanding of the kinetic fractionation and movement of water vapour from the Atlantic Ocean, which is being investigated in this study.

Liotta *et al* (2006) conducted a study using the stable isotopic composition of rainfall close in Italy to understand the origin and the orographic precipitation effects. The study used a comprehensive rain gauge network installed along the coast and inland to assess movement of air mass from the coast further inland. The study found that isotope signature along the coast at all rainfall stations were similar and changes slightly in land and significantly changes over hills. The study found that the water vapour produced by the Mediterranean Sea is characterized by high d-excess, but the high d-excess was coupled with other factors such as orographic clouds produce due to high diffusity than light isotope which produces enrichment of deuterium during droplet formation. Using modelling techniques of isotopes composition in clouds, a d-excess value of 45 was estimated. This study was used to understand the variation in rainfall isotopic composition from the ocean further inland and as an example of the continental and altitude effect on precipitation, this study also uses d-excess to explain the movement of air mass in a coastal region which is aids in describing d-excess values for this study.

Senturk *et al* (1970) conducted a study in semi-arid region in Turkey to determine groundwater residence time for an unconfined and confined aquifer. The study found that groundwater samples with low tritium activities between 0.2-4T.U reveal that groundwater is either with a system of a large volume that cannot be affected by precipitation entering the plain or that groundwater velocity is low. To determine which assumption is true, the ^{14}C age of deep groundwater will be younger at the recharge area. If the ^{14}C age does not differ considerably then the hypothesis is supported that groundwater velocity is very slow and the reservoir is recharges continental precipitations from the recharge area. According to Vogel (1970), low flow velocity is due to the fact that very little water can escape through the confining aquitard.

Chapter 3 - Description of the West Coast

3.1 Introduction

This chapter of the report will describe the physiographic information of the study area which includes topography, drainage, climate, hydrology, geomorphology and geology. These physiographic features control the location and timing of recharge at a site and therefore impact the choice of technique for estimating recharge. A comprehensive understanding of the physiographic properties of the study area is the basis to form a conceptual model. The hydrogeological situation in WCAS is complicated due to the complex nature of the regional geology. Geological information provides key information about the occurrence of groundwater and recharge processes.

3.2 Description of study area and physiography

The study area is comprised of Cenozoic sediments between the towns of Saldanha, Langebaan, Velddrif and Hopefield in South Africa. The study area is 2000km^2. The topography is dominated by the underlying geology where wave-cut terraces are overlain by aeolian dunes. The landscape is generally flat and covered by sand plains, sand and vegetated dunes that reach a height of 100 mamsl and surface limestone ridges. Intrusive granitic plutons are responsible for raised koppies which reach heights of 450mamsl at the towns of Darling and Vredenburg. The topography is influenced by coastal climate, geology and hydrological environment in the vicinity. The land use is dominated by shrubland, low fynbos and large cultivated land. Built-up and industrial areas occur in the small towns of Saldanha, Langebaan, Velddrif and Hopefield. An open pit phosphate mine is located in the study area close to Hopefield.

3.3 Description of drainage and hydrology in the West Coast

The Berg River is the only perennial river in the study area with its flow derived from the Drakenstein and Franschhoek Mountains, approximately 285 kilometres to the east and lies in abroad flat plain with elevation less than 20 mamsl (Seyler *et al*, 2017; DWAF). The Berg River discharges north-westwards into the Atlantic Ocean near Velddrif and is located within the north-eastern boundary of the study area. The Groen and Sout Rivers and their tributaries which are situated on the eastern border of the study region are important non perennial rivers in the study area and drain northwards into the Berg River (Timmerman, 1985b; Seyler *et al*, 2017). The Berg River is also supplemented by runoff contribution from low permeability Vredenburg Koppies

(Umvoto, 2008). A portion of the LRAU groundwater flows in a northerly direction towards the Berg River.The drainage region forms part of the Berg River Catchment and consists of 1 surface water quaternary catchments. According to Seyler et al (2017) according to weir data the Berg River in study area shows typical annual fluctuations of 1.6 in river between winter and summer months. The lower course of the Berg River is subject to tidal action and contains saline water during summer months.

The Langebaan lagoon which covers an area of 57 km^2. The Langebaan Lagoon has been classified as a wetland of international importance in terms of the RAMSAR Convention (1975), mainly because it supports more birdlife than any other wetland in South Africa (Saayman *et al*, 2003). The lagoon is surrounded by vegetated dunes which are natural recharge areas. The Langebaan Lagoon is an extension of the Saldanha Bay and the southernmost edge of the Lagoon is known as Geelbek. At Geelbek the average depth is 1-2m. Tidal fluctuations occur between the lagoon and Saldanha Bay. The shallow nature of the lagoon at Geelbek results in high temperatures (14°C in winter and 25°C in summer months) which results in high evaporation rates and greater salinity than in the Saldanha Bay. The Elandsfontein primary aquifer unit probably discharges into the overlying dune areas are like to store groundwater which could discharge into the southern end of the lagoon (Saayman *et al*, 2003; Weaver &Wright, 1994).

3.4 Description of vegetation in the study area

There are three terrestrial vegetation types that can be discerned in the West Coast, namely: West Coast Strandveld, Coastal Renosterveld and Cape Macchia (Saayman *et al*, 2003). The composition of vegetation is strongly controlled by the different soil sources of unconsolidated and consolidated aeolian sands, limestone and granites. These communities' grade into freshwater marshes dominated by *Phragmites* and *Typha* and then into salt marshes characterised by varying abundances of *Arthrocnemum* (*Salicornia*), *Juncus kraussii*, *Chenolea*, *Limonium, Spartina* and a mixture of other sedges and shrubs (Saayman *et al*, 2003; O'Callaghan 1994). Growth of the reeds *Phragmites australis* and *Typha capensis* on the shoreline surrounding Langebaan Lagoon provide clear evidence of the significant influx of groundwater to the Lagoon, because these plants can only survive in water or damp soil and hypersaline conditions (Clark *et al*, 2018).

3.5 Climatic description of the West Coast

The West Coast experiences a Mediterranean Climate with warm dry summers and cool winters. The study area is considered as semi-arid as evaporation exceeds rainfall (Seyler *et al*, 2017). The area receives a winter rainfall with August the wettest month throughout the year. The summer months in the study area range from late November to April. The highest measured temperature is in the month of February. Rainfall is of cyclonic nature extending over a few days with significant periods of clear weather in between. Precipitation is generally in the form of frontal rain approaching from the Atlantic Ocean. Mean Annual Precipitation (MAP) varies from 100-500mm in the region with most of the region experiencing an average rainfall of 280mm. According to Seyler *et al* (2017), the inter-annual variability and the variation between weather stations are significant. This can be seen in the comparison between South African Weather Station (SAWS) Rain Gauges located at the coast and further inland where significant differences of ±30% can be seen further inland. The data collected from the South African Weather Services (SAWS) illustrates the inter-annual variability and the variation between weather stations at the coast and 15km further inland. The Geelbek weather station and Langebaan Airforce base station both are situated at topographic lows. Figure 5 and 6 illustrates that rainfall is highest at the coast during winter months and that minimum and maximum temperatures are highest further inland. Rainfall occurs in the winter months (June-August) and rainfall decreases from south to north and from east to west, where some orographic rainfall occurs (Timmerman, 1985b). Evaporation rates are highest in the southern portion of the study area compared to northern region close to Vredenburg Mean where Mean Annual Evaporation at 2300mm/a. Figure 7 illustrates the inverse relationship between relative humidity and temperature. Relative humidity is high in region in winter months than in summer months in region and highest at the coast due to effects of excess oceanic water vapour.

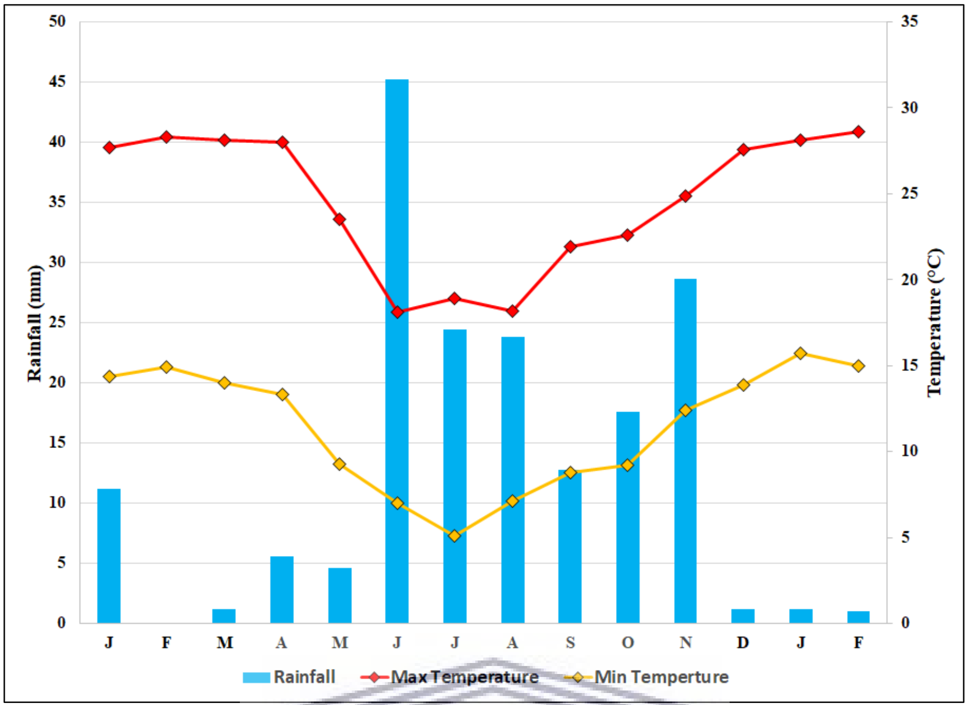


Figure 5: Rainfall and minimum and maximum temperature at Langebaan Airforce Base (SAWS)

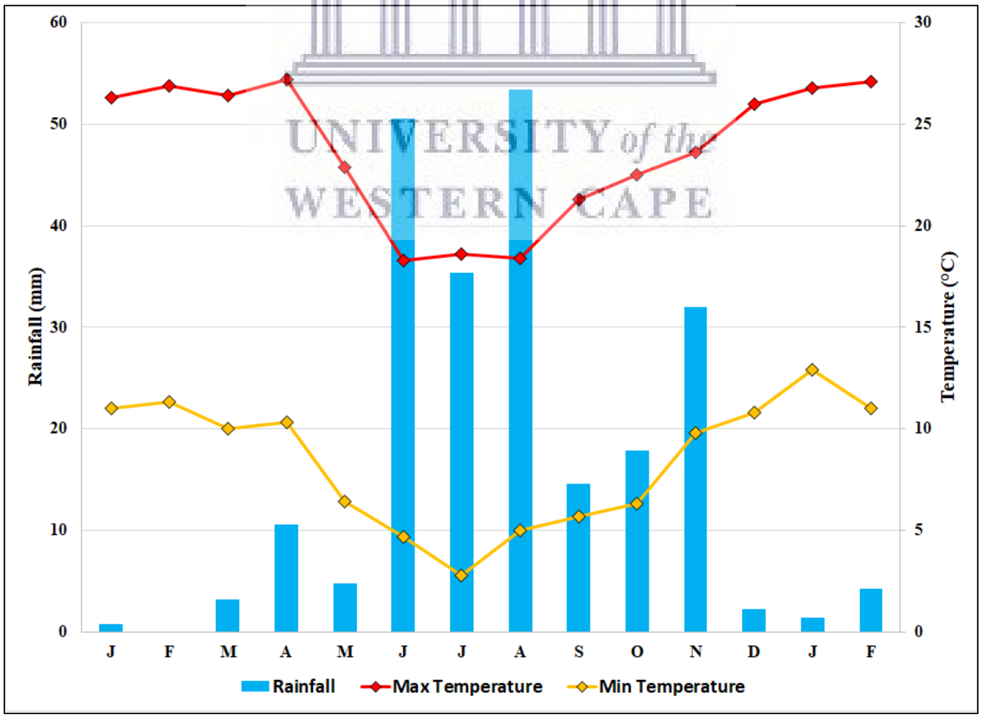


Figure 6: Rainfall and minimum and maximum temperature at Geelbek (SAWS)

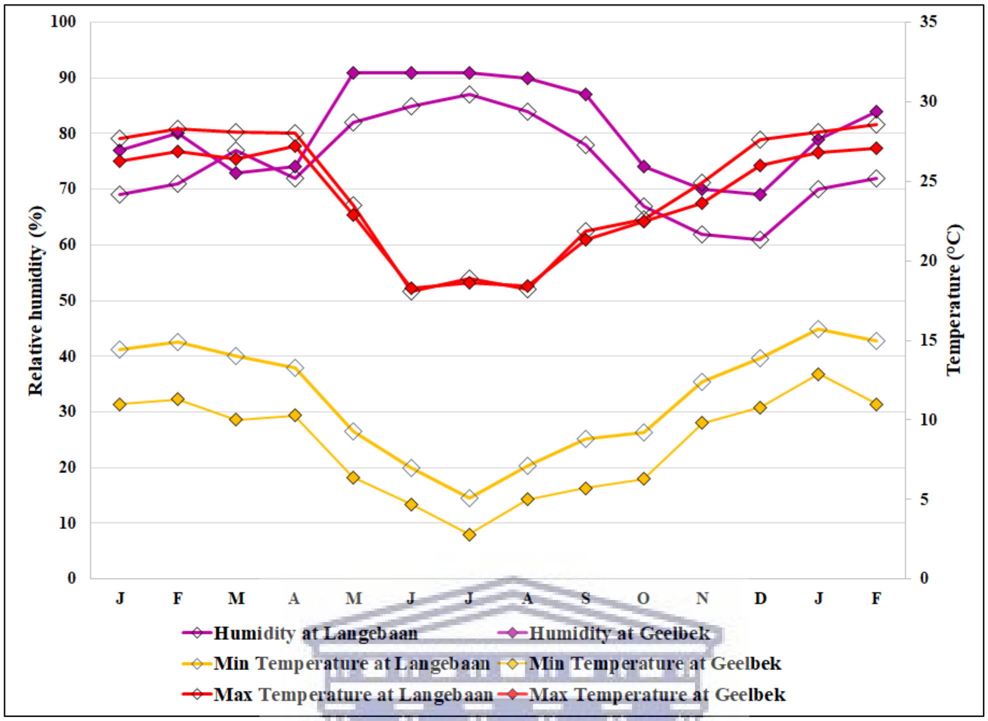


Figure 7: Measured relatively humidity at Langebaan Airforce Base and Geelbek. (SAWS)

3.6 Geology of the study area

The predominant geology of the region is composed of semi- to unconsolidated Cenozoic sediments of the Sandveld group (65Ma to present) which lie unconformably over the metamorphosed shale of the Malmesbury group and the granites of Cape Granite Suite. Figure 8 illustrates the geological confirmation table 2 shows the full stratigraphic sequence of the region. The formations that exist in the study area are the following: the Witzand, Langebaan, Springfonteyn, Varswater and Elandsfontyn.

The deeply weathered shales of the Malmesbury group underlie the younger sediments of the Sandveld group in the northeast, while the Vredenburg and Darling plutons of the Cape Granite Suite underlie the catchment in the south west. The Malmesbury Shale is of Pre-Cambrian age and outcrops in the valley of the Modder River and Berg River. These plutons dominate the topography and geomorphology whilst the rest of the area is characterised by low lying granitic hills. The Darling and Vredenburg granitic plutons are two successive intrusions of early Cambrian age.

The fluvial Elandsfontyn formation occurs within the deep areas of bedrock depressions and the paleochannels. The Elandsfontyn formation and is poorly sorted, angular, fine to coarse grained sand and gravel. The upper layer of the Elandsfontyn formation includes a significant clay layer which reaches a thickness of 50m in the study area. The Varswater formation overlies the Elandsfontyn formation and is composed of marine deposits with very fine to medium grained sand and coarse beach gravel. The Velddrif formation is of marine origin and is composed of poorly consolidated intertidal beach sand. The Langebaan, Springfonteyn and Witzand formations are of aeolian origin and vary from consolidated to semi-consolidated to calcareous dune sand.

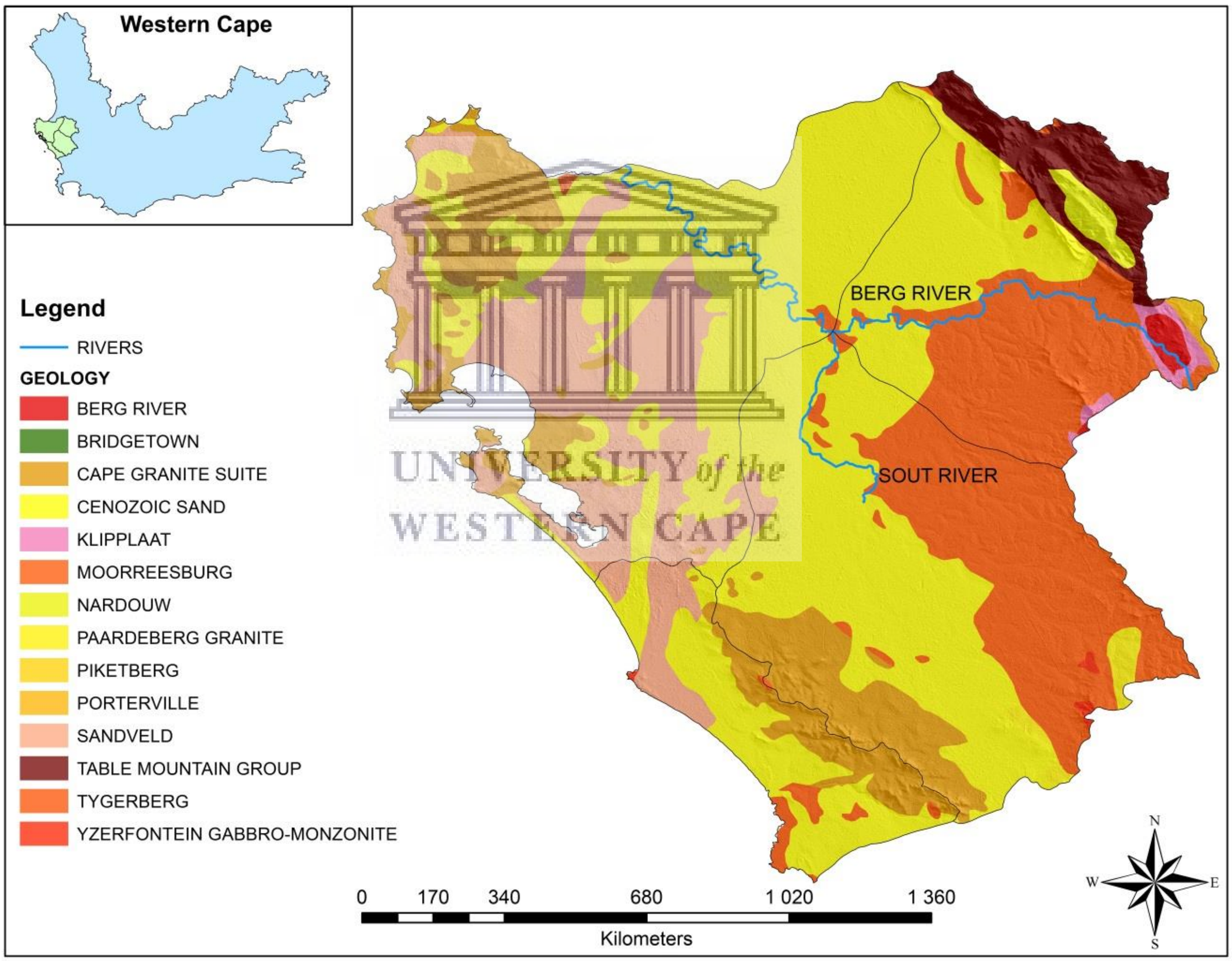


Figure 8: Geology of the West Coast

Table 2: Stratigraphy of units present in the West Coast (Seyler *et al*, 2017)

Age range (million years ago)	Group	Formation	Origin	Description
0 – 2.5	Sandveld	Witzand	Aeolian	Semi consolidated calcareous dune sand
		Springfontyn	Aeolian	Clean quartzitic sands, a decalcified dune sand. Dominates in the coastal zone
		Langebaan	Aeolian	Consolidated calcareous dune sand. The Aeolian deposit accumulated during the last glacial lowering of sea level when vast tracks of un-vegetated sand lay exposed on the emerging sea floor
		Velddrif	Marine	Beach sand. Associated with the last interglacial sea level rise with 6-7 m above present level
2.5-25		Vaarswater	Multiple sedimentary settngs: shallow-marine, esturine, marsh and fluvial.	Deposits include a coarse basal beach gravel member, peat layers, clay beds, rounded fine to medium quartzes sand member and palatal phosphate rich deposits.
		Elandsfontyn	Fluvial	Coarse fluvial sands and gravels, deposited in a number of palaeochannels filling depressions. The upper sections of the Formation include clays and peat.
			Major unconformity	
>495	Cape Granite Suite			Granites
	Malmesbury Group			Metamorphosed shales

3.7 Depositional history of the West Coast

About 25-2 million years ago in the Neogene, marine transgressions caused the granite dominated topography to flood. This caused the mouth of the Berg River, which was at Geelbek Lagoon to shift clockwise clock-wise then northwards during rise and fall of sea of the Atlantic Ocean. The fluvial deposition of basal gravels filled the granite and Malmesbury bedrock depressions before being overlain by phosphate rich marine sediments. During the Pliocene the mouth of the Berg River continued to shift northwards which is evident by the evolutionary changes in fauna. The depositional processes changed from erosive fluvial processes to aggregational aeolian processes. This depositional process is characterised by the presence of limestone and calcrete lenses due to remains of marine fossils. This caused river systems to dam and diverge their flow in lower reaches. The LRAU and EAU are paleo-courses of the Berg River. An understanding of the depositional history of the WCAS can ascribe groundwater age and residence time of groundwater in the region.

3.8 Geohydrology of the West Coast Aquifer System

The stratigraphy presented in Table 2 illustrates the complex hydrostratigraphy of the WCAS which varies in permeability and clay layers. The occurrence of groundwater can be classified into four geohydrological units. The bedrock aquifer is the deepest water bearing unit. The basal gravel of the Elandsfontyn formation forms the southern paleochannel called the Elandsfontein Aquifer Unit (EAU) and the northern paleochannel is called the Langebaan Road Aquifer Unit (LRAU). The clay layer of the Elandsfontyn formation forms the aquitard which superimposes the LRAU and EAU and confines these units. The EAU and LRAU are collectively known as the lower aquifer unit (LAU) of the West Coast Aquifer System (WCAS). The consolidated sands and calcrete with interbedded clay of the Sandveld group form the regional unconfined upper aquifer unit (UAU). The assumption that the complex geological setting is represented by four hydraulic layers is supported by preliminary exploration drilling (Timmerman, 1985) and more recently by numerical modelling investigations by Seyler *et al* (2017).

The basal gravels of the EAU and LRAU paleochannels reach a height of -5mamsl (Seyler *et al*, 2017) due to the basement rise to 0mamsl. There is negligible hydraulic connection between the LRAU and Eau due to the basement between the two paleochannels. The paleochannels extend towards the coastline and discharge into the Atlantic Ocean. The clay aquitard is distributed along the entire area of the West Coast Region and is the thickest at the centre of the LRAU and EAU close the Langebaan Road Wellfield. The clay layer varies in thickness regionally and in places excess 40m and can be less than 5m in other places as the clay layer seems to have been eroded for distance much greater than 5km from the coastline (Seyler *et al*,2017). The UAU can be considered as a single unconfined aquifer. The aquifer is known known to be a single succession of up to 4 aquifer-aquitard layers. These arenaceous sediments are usually 10-30m north of the Berg River and reach a thickness of more than 100m south of the Berg River at Anyskop.

The water table is deepest in the basement aquifers and similar in the UAU and LAU with the LAU slightly deeper (Seyler *et al*, 2017). The range of water levels is greatest in the basement aquifer at 2.5m a relatively low in both the LAU and UAU at 0.6m and 0.7 respectively. Seyler *et* *al* (2017) evidenced that the water levels of each aquifer unit correlate well with surface topography. Therefore, it can be assumed that at regional scale a hydraulic connection exists between the different aquifer units and that it is possible for groundwater to flow from the basement aquifer to the LAU and towards the UAU and vice versa. The groundwater flow is shown by the piezometric map Figure 9 which illustrates the correlation between water table and the topography. Groundwater flows for the unconfined aquifer flows from the water level high located close to Hopefield in a semi-radial direction towards the Langebaan Wellfield and then towards the Berg River and Saldanha Bay in the worth west and to the Langebaan Lagoon in the south west. The Berg River serves as a zero-flow boundary and separates the UAU of the north and south of the Berg River. The flow in the EAU and LRAU is controlled by the basement topography. Where the gravels of the Elandsfontyn formation are deposited concentrating flow along the axis of the LRAU and EAU paleochannels towards the mouth at the southwest coastline.

The hydraulic conductivity of the upper aquifer ranges from 8-24m/day (Parsons and associates, 2014). Storativity values of 0.13 are given (WCDM, 2009). The confined aquifer Elandsfontyn formation has a wide range of hydraulic conductivities 2-69m/day, transmissivity values between 22-3700m2/ day and storativity values of 0.0036 (Timmerman, 1985). The hydraulic conductivity of the Elandsfontyn gravels are higher in the LRAU than in the EAU. Timmerman (1985) cautioned that large-scale abstraction and exploration of the Elandsfontein formation, due to its superior hydraulic characteristics will cause indirect leakage from the unconfined aquifer. Due to recent wellfield development at Langebaan Road, high yielding fractures in the Malmesbury basement are being targeted which drain groundwater from the underlying aquifer (Seyler *et al*, 2017).

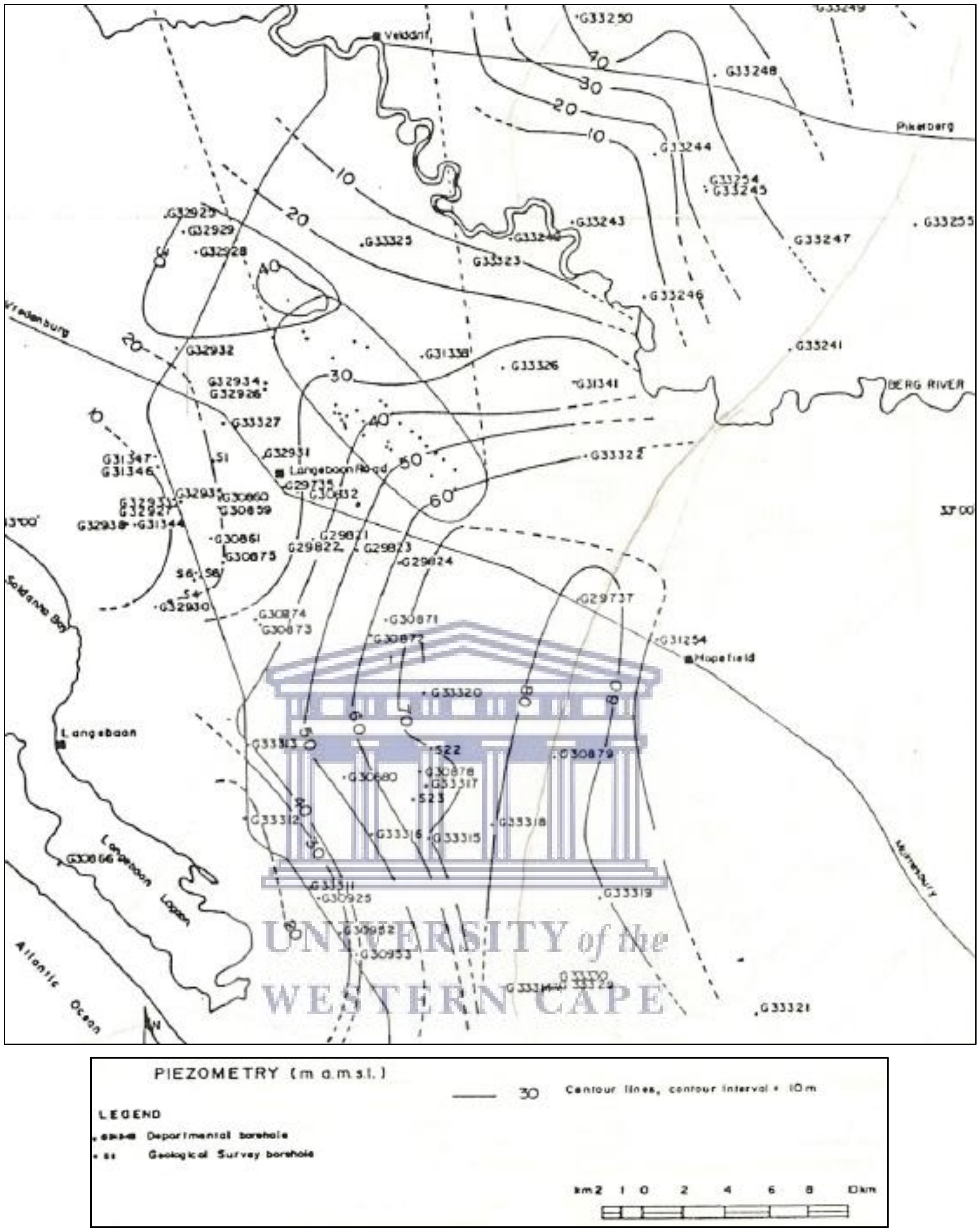


Figure 9: Piezometric Map of the LAU from observation boreholes (Talma and Tredoux, 2009)

3.9 Recharge mechanism for the West Coast Aquifer System

Recharge occurs naturally to the UAU from rainfall throughout the total area of the region. The sediments of the UAU have low permeabilities and large rainfall events recharges the UAU. Focused recharge is postulated to occur where contacts with granite koppies occur in Darling and Vredenburg due to enhanced runoff over these impermeable surfaces.

The recharge mechanism is more complex for the LRAU, EAU and basement aquifer due to lack of the Elandsfontyn and thick clay lenses that outcrop in the region. Timmerman (1985) suggest that the LAU is recharged through downward percolation or leakage at topographically high areas were rainfall rate is highest, clay layer is thinnest, and the water level is higher in UAU than in the LAU (Figure 9). These conditions make it ideal for groundwater to move from the UAU towards the LAU and flow laterally via under increasing pressure to the north and north-west via a piston flow mechanism (Seyler *et al*, 2017). This hypothesis is supported by immediate response in groundwater levels in the LAU in 1977 and 1983 after high rainfall events. The recharge mechanism to the bedrock aquifer is still not clearly known. It has been hypothesised that the source of groundwater is derived from the Franschhoek Mountains via deep incised fracture network (Weaver & Talma, 2005). According to Weaver & Talma (2005) recharge to the bedrock aquifer is a local phenomenon.

The WCAS is penetrated with a significant number of boreholes. Timmerman (1985b) has noted that many of the boreholes do not have adequate casing and could have collapsed due to poor borehole construction. It is possible that these uncased and collapsed boreholes may facilitate flow and create a hydraulic connection between the LAU and UAU and LAU and bedrock aquifer.

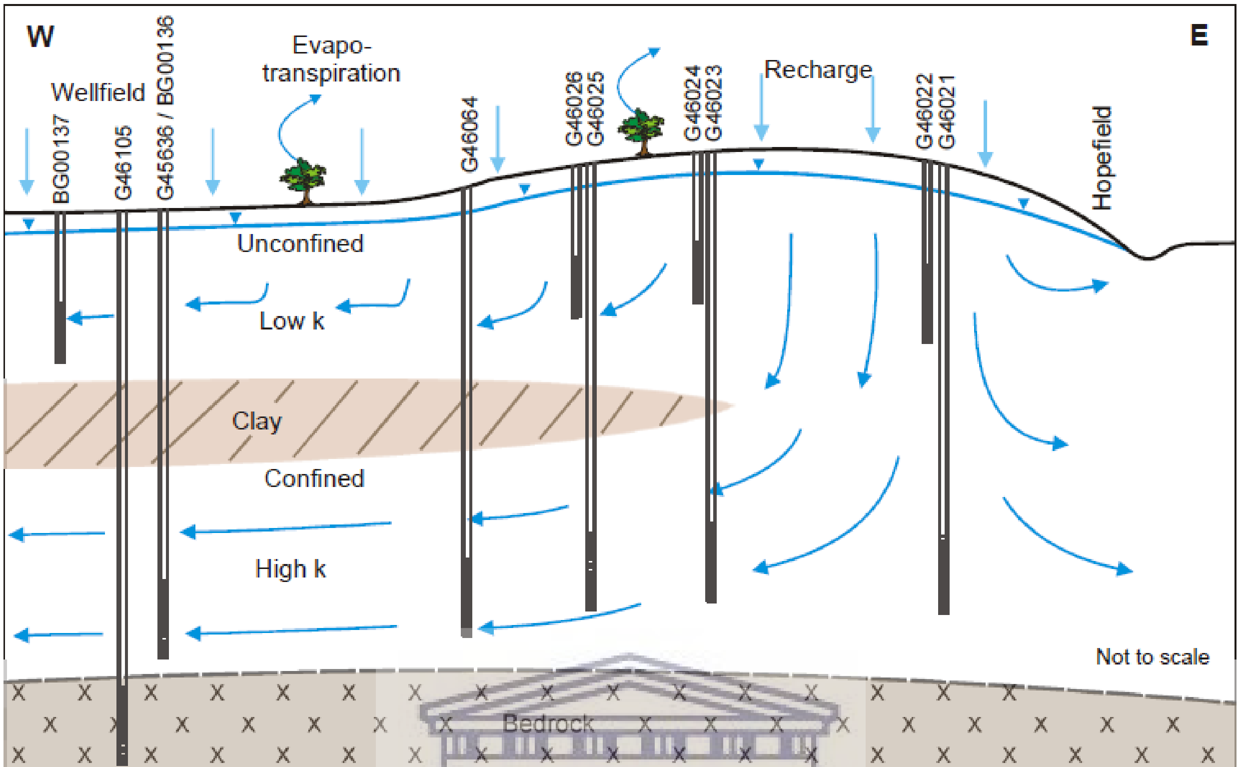


Figure 10: Conceptual model of recharge mechanism in the West Coast Aquifer System (Talma & Tredoux, 2009)

3.10 Surface Water- Aquifer Interaction for the West Coast Aquifer System

The groundwater contribution to baseflow is considered negligible for the region. The piezometric map (figure 9) showing flow towards the Berg, Sout and Groen Rivers coupled with relatively shallow water levels indicates that there is a hydraulic connection between groundwater of the LAU and UAU and surface water in the region. Groundwater is expected to occur as coastal discharge is the main mechanism for discharge for the LAU.

In the event when the Berg River is in flood and experiences high flows, the gradient will be reversed and the Berg River will experience losing conditions and recharge the LAU locally (Seyler *et al*, 2017).The pressure effects of the fluctuations in the river stage are detectable in the water levels in the upper aquifer unit. The effects of this pressure wave are present in borehole G33323, situated 1.5km away from the Berg River. G33323 displays a yearly cyclic fluctuation of 0.8m not related to rainfall but is the result if pressure variations caused by fluctuating river stage.

Chapter 4 - Research Methodology and Design

4.1 Introduction

This chapter of the report will describe the research design of the investigation and methodology that will be applied to achieve the aim. The research design is influenced by objectives of this study which provide answer to the research question. The research design utilized the relevant literature and attempts to provide explanation for the development of the hydrogeological conceptual model. The purpose of this chapter is to convey the research set-up which is an attempt to conceptualize recharge in the West Coast Aquifer System. This chapter will serve template to inform future research that will attempt the use of environmental tracers to conceptualize groundwater recharge in coastal aquifers. This chapter concludes with establishing quality assurance, limitations, and ethical considerations when undertaken during this study. This is done to encourage validity and reliability of this report. The methodology includes all procedures and techniques for acquiring and analyzing data.

4.2 Research Design

4.2.1 Research Design Approach

The study followed the quantitative experimental design approach and case study approach informed by a comprehensive peer review of publications concerned with the application of environmental tracers and groundwater recharge in terrestrial and coastal hydrogeological settings. This type of research allows the study to understand recharge mechanism and describe hydrogeological processes and its interaction with hydrological and meteorological aspects. The study attempts to create an in-depth analysis of environmental tracers and its suitability to elucidate recharge mechanism which infers the case study approach. The study involved the hydrochemical sampling of surface water, rainwater and groundwater are components of the hydrological cycle of which groundwater recharge is an aspect of. Hydrochemical sampling was done so that concentrations of Oxygen-18, deuterium, tritium, carbon-14 and chloride could be determined from different hydrogeological units using laboratory analytical techniques. The hydrochemistry will be used to provide concentrations of environmental tracers which will be used to qualitatively and quantify recharge mechanism and conceptualize groundwater recharge system for the West Coast Aquifer System.

4.2.2 Selection and description of the study sites

The boreholes that are used in this study are existing boreholes drilled in 1974-1985 by the Timmermans. The boreholes were drilled to provide insight into the geology, structural and hydraulic features of unconsolidated sediments and weathered bedrock. Boreholes were selected to elucidate recharge mechanism to the unconfined aquifer (Sandveld formation), to the confined aquifer (Elandsfontyn formation) and the bedrock aquifer (Malmesbury Shale). This was an important criterion to draw comparison of dominant recharge processes. Figure 11 illustrates the sampling locations for this study.

In an attempt to understand groundwater recharge, groundwater monitoring sites were selected based on their proximity to rain gauges. Groundwater and surface water samples were collected on a quarterly basis from 15th May 2017-20th February 2018. To conceptualize groundwater recharge, it was important to select experimental groundwater monitoring sites from the upper middle and lower parts of the West Coast Aquifer System. For the unconfined aquifer the upper aquifer was sampled from the high elevation areas close to Hopefield (G46024, G33502C, G33315 and G33505), the middle part of the unconfined aquifer (G46060, BG00137, G46028, G33316VL2) and the lower part of the unconfined aquifer (G33323, G46106, G46092 and BH1). For the EAU samples were collected in the upper aquifer (BG00074, G33505B and G33317) and in the lower aquifer (BH2). For the LRAU samples were collected from the upper aquifer (G46023) and the middle aquifer (G46059, G46029 and BG00136). The bedrock aquifer was also sampled (G46105,G46030 and G33502A).For the assessment of groundwater surface water interaction the Berg River and Geelbek Lagoon were sampled. Samples were collected from downstream the Berg River to assess temporal variation in isotopic composition from the only perennial river in the region and the extent of interaction between the Berg River and the WCAS.

Access to sample sites had to be relatively easy with an off-road vehicle as boreholes situated in remote areas in the Elandsfontein mine and in Langebaan road boreholes were situated close to roads or on private cadastral farms which made them easily accessible. The study sites chosen for the present study were chosen based upon the continuity of groundwater level data, distance of boreholes from rain gauges, rain gauges which are in working condition with continuity in rain gauge data.

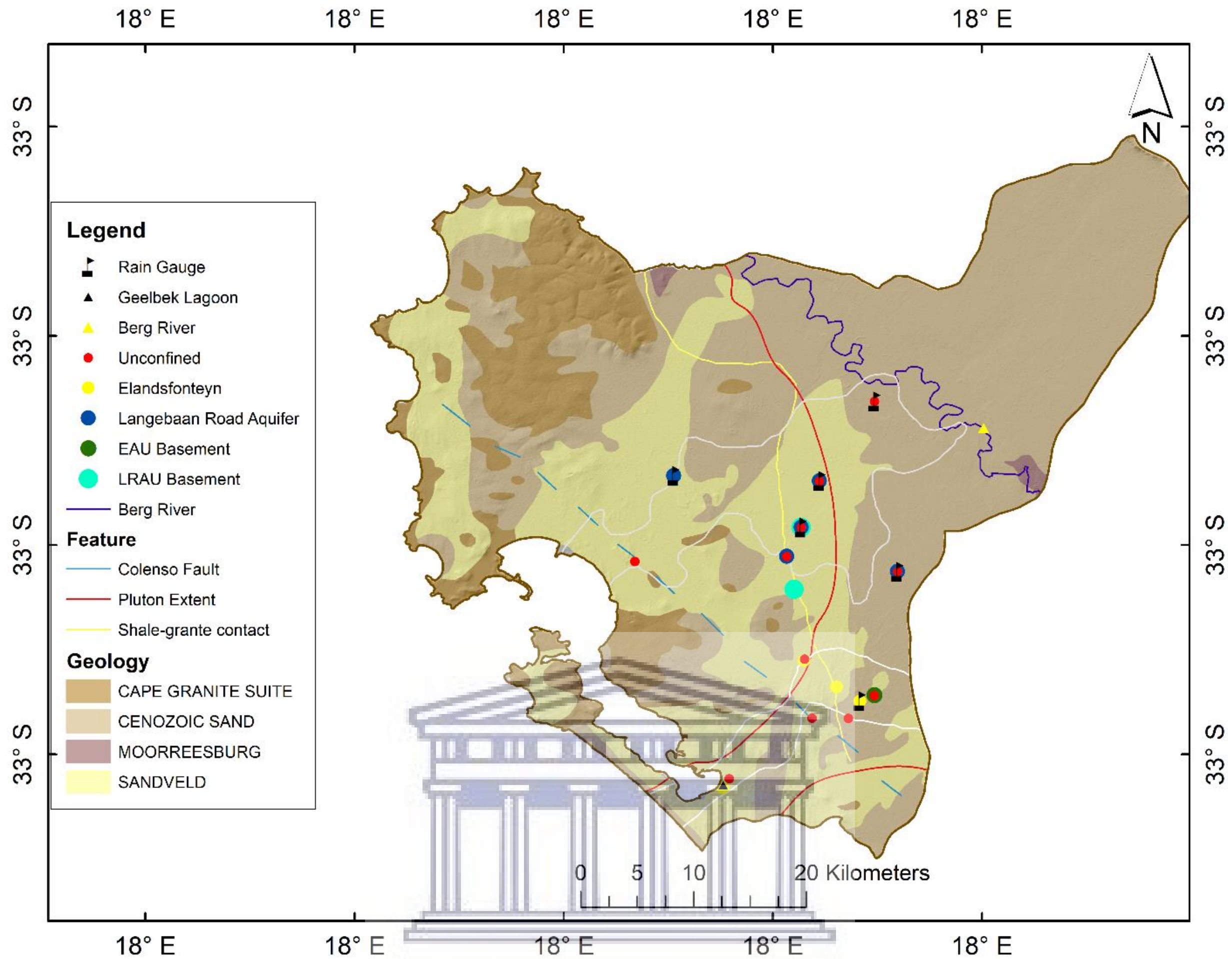


Figure 11: Groundwater, surface water and rainwater sampling locations throughout the West Coast

4.2.3 Analysis of study population and unit of analysis

The study used rivers, lagoon, rain gauges and boreholes of the within the upper, middle and lower parts of the West Coast Aquifer System. The Berg River and Geelbek Lagoon are boundaries of the WCAS which were included in the study to assess the surface-groundwater interaction within the study area. The reason for selecting the study population was to use the WCAS to demonstrate the application of environmental tracers to conceptualize groundwater recharge system in a coastal hydrogeological setting. The WCAS was used as a case study to demonstrate the suitability of using the contents environment tracers in different water samples, which is the unit of analysis for this study.

4.3 Data Collection Methods

At each selected site groundwater, surface water and rainfall samples (n=239) were collected on a quarterly basis during wet winter season (May and August 2017) and during the dry summer season (November 2017 and February 2018) for stable isotope and chloride analysis. Tritium and carbon-14 were sampled at each selected groundwater monitoring site (n=30) once during the data collection period during the wet winter month of August 2017. A tritium sample (n=1) was collected from a rain gauge located just outside the study area in the Aurora-Piketberg Hills in Aurora in August 2017.

4.3.1 Groundwater

Groundwater samples were collected from selected boreholes following the low flow/low stress purging method. Before sampling commenced borehole, logs were consulted from the DWS National Groundwater Archive (NGA) to determine where the submersible pump should be positioned in where the screen is located. The borehole is then purged for 15 minutes to remove any stagnant water. The depth that the pump is placed and the purging at a low speed that the drawdown of the water level is minimized, the mixing of stagnant water with fresh water from the aquifer is reduced which ensures that groundwater that is sampled is representative of the aquifer unit (EPA, 2017; Weaver et al, 2007). The electrical conductivity, pH and temperature were monitored as water was discharged from outlet pipe using a Martini Mi 806 multi-meter probe which was calibrated daily. New bottles were used for each monitoring period. A 50ml PET bottle with inset cap was used to collect a water sample for stable isotope analysis, 1L PET bottles were used to groundwater samples for tritium and chloride analysis and bottles were filled completely before closing with the screw cap. Water samples were collected straight from the outlet pipe. The water samples for sampled for environmental isotopes and chloride do not need to be acidified. All samples were labeled and stored into a cooler box and stored at ±4°C to limit the fractionation of fractionation and or biological impacts. The water samples were transferred to a refrigerator before analysis. Stable isotope samples remained at the Department of Earth Science at UWC and chloride samples were dispatched to the CSIR Laboratory in Stellenbosch.

The drum precipitation method was used for collection water sampled for radiocarbon analysis. Sampling for groundwater radiocarbon was done in August 2017, after initial hydrochemical sampling was done in May 2017. Based on the low alkalinity 100-liter samples were collected to obtain ±2g of total dissolved inorganic carbon (CO_2, HCO_3 and CO_3) (TDIC) to enable the analytical laboratory to have a sufficient TDIC for radiocarbon analysis. Groundwater is discharged from the outlet pipe into a two 50L drums attached with stopcock. At groundwater monitoring sites the pH of groundwater was raised by adding NaOH solution and 400g of $BaCl_2$ added. After the precipitation of barium carbonate, the supernatant was decanted and the carbonate slurry collected in a 1L PET bottle and dispatched with all tritium samples to iThemba Laboratory in Johannesburg.

4.3.2 Rainfall

Cumulative rainfall samples were collected via permanent rainfall collectors previously installed by DWS which is located at close proximity (<1m-25m) to groundwater monitoring sites. Rainfall was sampled in August, November 2017 and February 2018. The rain gauge had spikes placed on top of the collector to discourage birds from sitting on the rim and adding non-meteoric contributions to the gauge. The collectors are automated floating type rain gauges connected to a Perspex cylinder which is attached to a plastic discharge pipe. Rainfall measurements are taken by an automated logger which is calibrated quarterly, and the data is then downloaded by DWS officials whom is able to download rainfall for months where sampling did not occur. Rainwater was collected for stable isotope and chloride analysis when there was enough water in the collecting cylinder. The cylinder was emptied completely, and the data logger was reset after sample drained into respective sample bottles from a plastic pipe, to ensure that rainfall sampled was representative of rainfall events after the last sampling event. According to Diamond (2012) and Bosman (1981) metal rainfall gauges collect 7% more rainfall than standard plastic rain gauges, as metal rain gauges which are enclosed reduce evaporation effects on which can facilitates fractionation and alters environmental isotope composition and cause enriched δ^2H‰ and $\delta^{18}O$‰. Stable isotope samples remained at the Department of Earth Science at UWC and chloride samples were dispatched to the CSIR Laboratory in Stellenbosch. The rain gauge sampled to establish rainwater tritium activity in the West Coast was couriered to iThemba Laboratory in Johannesburg.

4.3.3 Surface Water

Surface water samples were collected from the Berg River and the Geelbek Lagoon. Stable isotope was only sampled from the surface waters using the grab sample method on a quarterly basis from May 2017 to February 2018.A bailor was used and lowered from a road bridge into the deepest flowing part within the channel. Once the bailor was filled beneath the water surface, the bailor was lifted quickly, and the sample was decanted into 50ml sample bottle. The lagoon sample was collected directly from a permanent pool which was located close to a footbridge. The sample was collected 10cm below the water surface. Surface water samples remained at the Department of Earth Science at UWC for analysis.

4.4 Data Analysis Methods for environmental tracer analysis

4.4.1 Stable isotopes

All stable isotopes analysis of groundwater (n=77), surface (n=5) and rainwater (n=12) were performed using the off-axis integrated cavity output spectroscopy (OA-ICOS) method at the Earth Sciences Department at the University of the Western Cape, Bellville, South Africa. The analysis of δ^2H and δ^{18}O values were analyzed relative to Standard Mean Ocean Water (SMOW). The results of the stable isotopic analysis are reported as delta (δ) values in parts per thousand (denoted as ‰ or permil) as defined by the following Equations 7 and 8.

$$\delta^{18}O = \left[\left(R_{sample} - R_{standard}\right) \div R_{standard}\right] \times 1000 \quad \text{Equation 7}$$

$$\delta^{2}H = \left[\left(R_{sample} - R_{standard}\right) \div R_{standard}\right] \times 1000 \quad \text{Equation 8}$$

Where:

R is the isotope ratio of the heavy to the light isotope (e.g. $^{18}O/^{16}O$) of the sample and the standard. For data normalization, the two standards were calibrated directly against VSMOW2 and SLAP2 international standard waters. The data were normalized to the VSMOW/SLAP scale.

Off line preparation was done before placing water samples into the autosampler. The samples were filtered using 0.25mS filter to a vial of 1.5 mL which is then sealed with a vial cap and placed into a vial tray. The laser spectrophotometer is highly sensitive to Volatile Organic Compounds (VOC's), Dissolved Organic Compound (DOC's), alcohol's and hydrocarbons which is why samples are filtered. The vial tray is then places in the sample prep device.

The analysis was performed on a LGR DLT-100 liquid water isotope analyzer (model 908-0008-2010) which was connected to a LC PAL liquid auto-sampler (model 908-0008-9001) for the simultaneous measurement of $^{2}H/H$ and $^{18}O/^{16}O$ ratios of groundwater, rainwater and surface water samples. The procedure made use of LIMS (Laboratory Information Management System) for Lasers 2015 (version 10.096) which was co-developed by the United States Geological Survey (USGS) and the International Atomic Energy Agency (IAEA). The auto-sampler was inserted SGE 5µl (model 5F-C/T-0.47/5C) for the injection process of the water samples into heated injector block which vapourized the samples as 85°C. The laboratory standards were analyzed with each sample batch. The analysis template procedure proposed by LIMS employs a distribution layout of several occurrences of two laboratory standards one which represents high-δ (Aqualle distilled water) and one which represents low-δ (Evian distilled water) a control standard, and water samples situated in-between these lab standards. Ten injections are done per sample which ensures the accuracy of results. The first four injections are ignore and taken as δ-values. This is done to overcome the influence of previous samples in the line by influencing δ-values of the sample being analyzed. The reported value I on the average of the last six injections.

The δ-values are graphically presented along the Global Meteoric Water Line (GMWL) by Craig 1961, Local Meteoric Water Line developed by Diamond & Harris 2008) developed for Cape Town and an evaporation which is represented as the line of best-fit of all groundwater samples. Comparison water samples relative to other samples and the GMWL, LMWL and evaporation can provide insight into the spatial and temporal aspects of recharge, possible recharge mechanism, identify sources of recharge and evaporative history as is illustrated in figure 12.

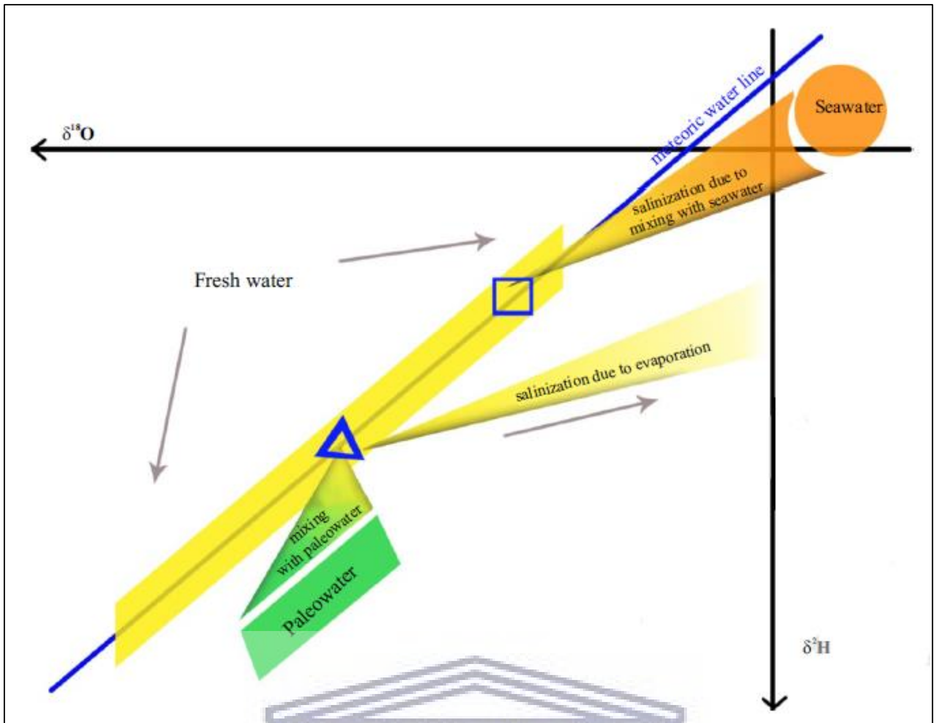


Figure 12: Qualitative interpretation of stable isotopes for groundwater recharge assessment due to several physical processes. (Satrio et al, 2017)

4.4.2 Tritium

The samples were distilled and subsequently enriched by electrolysis. The electrolysis cells consist of two concentric metal tubes, which are insulated from each other. The outer anode, which is also the container, is of stainless steel. The inner cathode is of mild steel with a special surface coating. Some 500 ml of the water sample, having first been distilled and containing sodium hydroxide, is introduced into the cell. A direct current of ±10–20 ampere is then passed through the cell, which is cooled because of the heat generation. After several days, the electrolyte volume is reduced to some 20 ml. The volume reduction of some 25 times produces a corresponding tritium enrichment factor of about 20. Samples of standard known tritium concentration (spikes) are run in one cell of each batch to check on the enrichment attained.

For liquid scintillation counting samples are prepared by directly distilling the enriched water sample from the now highly concentrated electrolyte. 10 ml of the distilled water sample is mixed with 11 ml Ultima Gold and placed in a vial in the analyzer and counted 2 to 3 cycles of 4 hours. Detection limits are 0.2 TU for enriched samples.

4.4.3 Radiocarbon

CO_2 is generated by acidification of the field precipitate with phosphoric acid (H_3PO_4). The CO_2 sample gas is transferred from the production/purification line into a 1 litre Pyrex flask, the pressure (610 mmHg max.) is measured on a manometer and this measuring volume isolated. 10 ml of Carbosorb is pipetted into a standard 20 ml low-K glass counting vial that is attached to the system through a vacuum-tight, flexible connection. Air is removed by opening the vial briefly to roughing vacuum. The CO_2 sample is then transferred quantitatively from the measuring volume by freezing with liquid N_2 into a small trap which forms part of a low-volume (~60 ml) section of the system. The trap is pumped to high vacuum to remove residual non-condensable gas. The small volume section is isolated, the tap to the vial opened and the CO_2 allowed to sublimate whilst the vial is shaken by hand. The rate of CO_2 absorption usually balances its release from the trap through ambient (~25°C) warming, at pressures around 300-400 torr. The rate may be controlled when needed by slightly heating the trap or briefly cooling it with liquid N_2.

Uncooled, the rate of absorption under these conditions causes the temperature of the Carbosorb in the vial to rise to 70°C. This does not seem to have any deleterious effect on the counting characteristics. However, the NH_4 released by the Carbosorb forms a gas "blanket" over its surface, through which the CO_2 has to diffuse, the absorption rate dropping to near-zero at an equilibrium pressure of some 150 torr. When the vial is kept cool in a water bath, the equilibrium pressure reduces to some 40 torr, implying more complete CO_2 absorption, due to lower NH_4 pressures above the Carbosorb surface.

The counting vial is removed from the vacuum system and 10 ml Permafluor+ is added. The vial is capped tightly and the cocktail shaken well before counting. Because of a considerable overlap between the pulse height spectrum of ^{14}C and the spectrum of ^{222}Rn, samples for radiocarbon analysis need to be stored for about three weeks in order to allow ^{222}Rn (t1/2 = 3.85 days) to decay to below significant levels. The prepared sample cocktails are therefore placed immediately in the cooled and darkened sample changing chamber of a Hewlett Packard TriCarb liquid scintillation spectrometer. After the ^{222}Rn intensity has sufficiently declined, samples are counted four times at four hours duration of each count. The results are expressed in percent modern carbon (pMC).

4.4.4 Chloride

A total of 95 groundwater and 10 rainwater samples were analyzed for dissolved chloride in water samples. Chloride analysis was conducted at the Council for Scientific and Industrial Research

(CSIR) in Stellenbosch. Determination of chloride in water samples was done by Flow Injection Analysis (FIA) Coloritric method. The method is based on the assumption that Chloride reacts with mercuric thiocyanate, liberating thiocyanate ion by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly colored ferric complex, and the absorbance is measured at 480 nm (CSIR, 2017). The instrumentation consists of The Flow Injection Analysis (FIA) System (OI Analytical Flow Solution® 3000) consisting of the 120-Place Autosampler Expanded Range, Photometric Detector with 5-mm path length flowcell, Chloride Cartridge (Part #A001568) and a 480-nm optical filter. The FIA uses Omnion software as a data acquisition system.

Table 3: Materials required for analysis of chloride using FIA

Materials
o 20ml syringes
o 0.45µm syringe filters
o test-tubes
o A grade verified 1L Volumetric flasks
o A grade verified 200ml Volumetric flasks
o A grade verified glass bulb pipettes (1, 2, 5, 10, 20, 50ml)
o Desiccator
o Analytical balance
o Grade 1 Milli-Q water with Electrical Conductivity of <0.01mS/m
o 69% AR Grade Nitric Acid

The elemental analysis of solutions is undertaken using reagents, water samples and quality control standards. The combined colour reagent is made of in a 500 mL volumetric flask, where 75 mL mixed of stock Mercuric Thiocyanate Solution is added to 75 mL Stock Ferric Nitrate Reagent and diluted to the mark with Milli-Q (deionized and degassed) water. Working calibration standards are prepared by using a pipette and individual volumes of the working stock standard into 200ml volumetric flasks are made-up to mark with Milli-Q water. SABS Watercheck synthetic samples are used for quality control standards and included in the analysis. The preparation of the solutions is followed as prescribed by the SABS proficiency study. Before analysis of dissolved chloride in water samples, the electrical conductivity of the sample is checked to make the appropriate dilutions as estimated by the table below. The sample is then filtered the through a 0.45µm filter using a 20ml syringe into the test-tube. The test tube is then placed into the sample rack along with the quality control standards ready for FIA analysis. The samples will be saved according to the date it is run and the number of the sequence of that particular day. FIA sequence analysis was commenced by clicking on the START button. The data exported from the Omnion software is opened up in Microsoft Word, as an RTF document, is then copied and pasted into Microsoft Excel as a Microsoft Word document object.

4.4.5 The Chloride Mass Balance Method

The chloride mass balance (CMB) technique is used as the primary method to quantitively assess groundwater recharge in this study area. This method was selected based on accuracy of using the method in a semi-arid region nature, the size of the size of the study area, cost effectiveness, first approximation of recharge and abundance of anion analytical facilities in the Western Cape. Furthermore, chloride is conservative due to its anionic form and makes chloride the only chemical-method that is used to estimate groundwater recharge. The CMB method was used in this study to assess the appropriateness of using the method to characterize and conceptualize groundwater recharge in an alluvial coastal hydrogeological setting, using the West Coast Aquifer System as a case study. The results of this study will provide an independent comparison to the recharge estimates obtained by previous investigations where chemical, physical and modelling techniques were applied. The method was chosen based on its strengths regardless of limitations regarding recharge estimation.

The CMB technique was used to estimate recharge on a local and regional scale using the saturated zone approach for the upper unconfined aquifer unit of the WCAS. The fundamental basis of the CMB method is that the water mass flux crossing the plane of the water table can be calculated it as long as most of the assumption is met based on equation 9. Groundwater recharge is therefore calculated as the product of the annual precipitation (mm) and weighted chloride concentration of precipitation (mg/L) as a proportion of the average groundwater chloride concentration (mg/L).

$$q = \frac{PCl_p}{Cl_{gw}} \qquad \text{Equation 9}$$

Where: q is the groundwater recharge flux (LT^{-1}), P is the average annual precipitation (LT^{-1}), Clp is the weigh average chloride concentrations in precipitation (ML^{-3}), and Clgw is the average chloride concentration in the groundwater (ML^{-3}). M represents mass, T is time and L, length; all in consistent units.

The weighted mean values of chloride concentration in rainwater were calculated by multiplying the annual precipitation amount prior to sampling (mm) with the chloride concentration in rainwater (mg/L) for the sample that was that day based on the following equation 10:

$$\sum = P \times Cl_p \qquad \text{Equation 10}$$

Groundwater and rainwater chloride data were obtained by the hydrochemical analysis of water samples which were sent to the CSIR Laboratory after quarterly data collection campaigns. Boreholes from the unconfined aquifer were used to estimate groundwater recharge based on the rise of water table after rainfall events. The method is not applicable to deeper confined aquifers due to longer groundwater travel times, for which this study only collected data for nine months which is not sufficient to estimate recharge deep groundwater systems.

The CMB technique uses site specific measurements to estimate groundwater recharge which will be representative of the groundwater added to storage during the data collection period. Rain gauge BG00074-RF was used to estimate recharge for the boreholes found in Elandsfontein Nature Reserve. G46024-RF was used to estimate recharge close to the town of Hopefield (G46024). G46105-RF was used to estimate recharge at the Langebaan Road Wellfield (BG00137). G33323-RF was used to estimate recharge at the floodplain of the Berg River (G33323) and located furthest north. G46059-RF was used to estimate recharge between the wellfield and the Berg River. G46092-RF is located closest to the Saldanha and was used to estimate recharge for a borehole at the Geelbek Nature Reserve.

Recharge estimates in coastal hydrogeological environments are not accurate due to the high chloride concentration in soils and groundwater as a result of marine regressions and transgressions. The high variability of chloride in rainfall very close to the sea as reason of non-rain deposition of chloride is another reason for the uncertainty in recharge estimates close to the coast. Due to these limitations and that not all assumptions are met, the CMB can be used as a first approximation of groundwater recharge (Adams, 2004; Bazuhair and Wood, 1996; Wood, 1999).

For the application of the CMB technique in this study, the following assumptions are made:

- The major source of groundwater chloride is precipitation.
- The alluvial unconfined aquifer receives main recharge by direct precipitation which infiltrates through the unsaturated zone.
- There are no external sources and sinks of chloride between the surface and water table.
- Chloride is conservative in the system.
- Steady-state conditions are maintained with respect to long term precipitation and chloride concentration in that precipitation.
- No evaporation of groundwater occurs upgradient from the ground water sampling points.

4.5 Quality Assurance

Describing recharge mechanism and estimating groundwater recharge cannot be measured directly, however measuring components of the hydrological cycle such environmental tracer content can provide insight into groundwater-surface water interaction, delineating origin of groundwater, evaporation and recharge history. In this study measurements of multi-environmental tracers were used to conceptualize groundwater recharge mechanism and estimate recharge for the WCAS. The hydrogeological conceptual model will provide information such as delineate recharge area and sources of recharge to aquifer units.

A huge concern of these laser-based instruments is its sensitivity to organic contaminants (VOCs, DOCs, alcohols, hydrocarbons etc.) present in water samples. Organic contaminants may enter the mirrored cavity of the LAS instrument causing spectral interference, subsequently producing erroneous and erratic stable isotope measurement results. LAS manufacturers (Picarro Inc. and Los Gatos Research Inc.) produced offline software that can be utilised to analyse post process sample runs. This is done by comparing the spectra of each sample to that of clean lab standard water. This software can therefore assist in identifying bad samples possibly having organic contaminants present and might potentially be corrected. These samples are identified and be removed and analysed by IRMS. To avoid possible processing of samples that might be contaminated, all runs are checked with LGR's Spectral Contamination Identifier™ software.

To ensure the reliability of the recharge estimation results from this study, the results were compared with recharge estimates of Weaver & Talma (2005), Conrad *et al* (2004) and Eilers (2017) which applied the same methodology to estimate recharge in the same study area. In order to ensure that the environmental isotope results were reliable the results of stable isotopes were compared to that of Weaver and Talma (2004) who investigated recharge mechanism in the WCAS, whereas the Keesari (2017), Satrio (2017), Ayadi (2017) and Kpegli *et al* (2018) are results from global studies that this study used for comparison.

To ensure the reliability of the results from chemical analysis of chloride many quality assurance measurements were undertaken to ensure the validity of the results. The analysis of chloride was conducted at the CSIR laboratory in Stellenbosch and the analysis of tritium and carbon-14 was die at iThemba laboratories, which are South African National Accreditation Systems (SANAS) accredited. These laboratories are inspected and provided with certification and undergoes rigorous testing and calibration control checks as it needs adhere Good Laboratory Practices Act (Act No.19 of 2006) in order to maintain accreditation.

4.6 Statement of ethical consideration

Groundwater and surface water monitoring sites selected for this study are all located on privately owned land. Permission was granted by farm owners, and management staff of the Geelbek and Elandsfontein Nature reserve prior to the commencement of the data collection activities. Permission was granted through verbal and written agreements between DWS and a hard copy of the agreement was always on hand as proof of agreement in order to avoid access to the monitoring sites being denied. Permission to use the meteorological data from the South African Weather Services (SAWS) was obtained for this study. A non-disclosure agreement serves as evidence of the agreement between the researcher and SAWS. Permission was granted through a written agreement between the researcher and CSIR and iThemba laboratory whom analyzed water samples for environmental tracer content. The data was from CSIR was granted as the researcher was working on a collaborative project with the institution. Groundwater samples were analyzed by iThemba Laboratory for free if the laboratory was acknowledged for all analysis and contribution made with current study.

Research being done makes use of secondary data provided by the Department of Water and Sanitation (DWS). The secondary data is the property of DWS and is important to understand discretion must be applied when using the data. It is important to respect the wishes or conditions DWS as to how data is used to maintain a good working relationship between DWS and academic institutions.

The benefits of doing research were communicated to the farmers through the DWS officials as the findings from the current study can provide scientific knowledge that could be useful to farmers and other stakeholders about water availability in the study area. The data collection period commenced during a period when groundwater abstraction restrictions were issued to farmers as a consequence of drought conditions being experienced in the study region. Therefore, it was important that farmers and nature reserve managers were made aware when groundwater sampling was conducted to avoid conflict and to establish good working relationship with all stakeholders. The study did not introduce any chemical substance into the environment that could have adverse impacts on people and the environment itself. All chemical waste substances used in the field were discarded into a labeled 25L drum to maintain zero ecological impact whilst data collection was done. No physical or chemical waste was discarded in the region to ensure that no change in the water quality of surface and groundwater occurred.

4.7 Limitations of the study

Limitations of the study constrain the efficacy and reliability of methodological approach undertaken to achieve the objective and aims of the study. The main limitation of the study was that the data collection period was confined to a very short period of nine months. It would've been beneficial to sample on a monthly basis for a period of two years. Groundwater recharge is a dynamic process as is weather in the study area. Therefore, a lengthened data collection period would allow the study to describe hydrological fluxes in extensively. Although the data collection period was short, sampling multiple environmental tracers for this study provided insight into recharge mechanism for the WCAS that no study has done before. This was a limitation as m using the CMB Method will provide time specific recharge estimation. Moreover, not using multiple recharge estimation methods proved to be a limitation as it would be useful to validate the recharge estimates obtained by using the CMB technique against other methods such as the Water Table Fluctuation Method,

The study was limited by the low rainfall that occurred during the data collection. Laboratory Standard Operating Procedure (SOP) requires that a particular volume of water is collected for analysis of environmental tracer. The low rainfall that occurred in the West Coast during the data collection period restricted the volume of rainwater samples that could be collected, and which environmental tracer could be sampled. Both the CSIR and iThemba laboratories require a 1L sampled for chloride and tritium respectively. Therefore, the volume of rainfall was often inadequate to collect a sample for chloride, stable isotope and tritium analysis. Therefore, a sample from rain gauge in Aurora was taken to establish what modern rainfall tritium activity of rainfall in the West Coast is.

This study was done as part of collaborative project between the University of the Western Cape (UWC), Council for Scientific and Industrial Research (CSIR) and the Department of Water and Sanitation (DWS). With the advice of collaborators sites were selected which was used for the present study. This became a limitation as the study applied an inductive research design approach, as sampling for tritium and carbon-14 groundwater monitoring sites were not extensive enough due to the selection of boreholes from the project team. If groundwater was sampled from available boreholes that were not included in the study, it could potentially provide greater insight into recharge mechanism where some gaps were identified in the study. It would be beneficial that the study takes a deductive research design approach to sample all groundwater monitoring sites for all environmental tracers at the same time throughout the entire data collection period.

Another limitation of the study the limited access to equipment due to a limited and restricted budget. Three different submersible pumps were used through the duration of the data collection period due to problems that were experienced during groundwater sampling which include electrical faults, submersible pump being wedged within the borehole casing and sediment being pumped consequently clogging the pump. Since the unit of analysis is environmental tracer concentration in surface and groundwater, it was imperative to secure a submersible pump in working condition so hydrochemical data could be obtained. A pump was secured from DWS which ensured that efficient data collection for the study was achieved.

Chapter 5: Describing recharge mechanism and groundwater residence time by using stable (^2H, ^{18}O) and radiogenic isotopes (^3H, ^{14}C)

5.1 Introduction

Chapter 5 of this study presents and discusses the results which were obtained during the assessment of recharge mechanism within the West Coast Aquifer System. This chapter addressed objective 1 of the study, which focused on applying environmental isotopes to understand the source of recharge, define groundwater flow, describe groundwater surface water interaction, trace and confirm groundwater residence time which provide insight and describes the how the hydrological cycle influences recharge mechanism in a coastal setting. The central argument in this chapter was that if the regional spatial and temporal distribution of the environmental isotopes of different sources of water were understood, then the conceptualizing the recharge mechanism in the West Coast would be possible for effective groundwater resource management.

5.2 Key results: stable isotopes

5.2.1 Rainwater

To establish trends in rainfall stable isotopic signatures a plot of rainwater $\delta^{18}O$ and δ^2H data is presented in Table 4. From the analysis $\delta^{18}O$ values for rainwater ranged from -2.85 to 0.55‰ with a mean of -1.34‰ and a standard deviation of 1.04‰. The δ^2H values ranged from -6.3 to -4.4‰ with a mean of -2.08‰ and a standard deviation of 2.97‰. The d-excess values ranged from 0.00‰ to 17.5‰ with a mean of 9.39‰ and a standard deviation of 5.42‰. The outlier is δ^2H at rain gauge G33323-RF with a measured δ^2H of 1.2‰.

Table 4: Statistical summary of stable isotopes of rainwater samples (n =12)

	$\delta^{18}O$‰	δ^2H‰	d-excess
Min	-2.85	-6.3	0.00
Max	0.55	4.4	17.5
Mean	-1.34	-2.08	9.39
Std deviation	1.04	2.97	5.42

Figure 13 illustrates that rainwater isotopic composition in the West Coast correlate well with seasonal effects in the West Coast. The observed isotopic composition of rainwater in the West Coast is mostly negative in the winter months (August) with a range of -6.3‰ for δ^2H and -0.8‰

for $\delta^{18}O$ and becomes more comparatively more positive in the dry summer months with a range of 4.4‰ for δ^2H and 0.55‰ for $\delta^{18}O$ as sample period progressed. During the rainy season, rain gauge G46059-RF experiences most negative rainfall isotopic values at -5.3‰ for δ^2H and -2.85‰ for $\delta^{18}O$ whilst rain gauge G46092-RF experiences the most positive rainfall isotopic values at -2.87‰ for δ^2H and -0.87‰ for $\delta^{18}H$ which can be seen in figure 14. . The spatial distribution of $\delta^{18}O$ values is illustrated in figure 16.

Maximum d-excess value was recorded in at G46059-RF in the rainy season and the lowest was 0.00 which was recorded at G46105-RF in the month of February. Therefore, it is evident that lighter isotopes dominate rainfall in the rainy winter months than in the summer. Generally, seasonal variations were also observed in the deuterium excess values. At most rain gauges, deuterium excess seems to decrease as rainfall events decreased. Rain gauge G46105-RF was the only rain gauge monitored that deuterium excess increased in November to 11.3 from 4.26 in August and then decreasing to 0.00 in February 2018. The spatial distribution of d-excess values is illustrated in figure 17.

The stable isotopic composition of rainfall shows a definite decrease in heavy isotopes with an increase in rainfall amount of $\delta^{18}O$ (Figure 14). This correlation seems to be strongest for $\delta^{18}O$ with a R^2-value of 0.62 which indicates a weak direct relationship. Comparatively a weaker correlation exists for δ^2H with R^2 value of 0.17. The deuterium excess shows a stronger direct relationship with rainfall than δ^2H, as the deuterium excesses increases with increasing rainfall amount ($R^2 = 0.45$). This suggests that rainwater $\delta^{18}O$ values decrease from the coast to the interior. This may be due to the altitude effect and the process of rainout whereby the $\delta^{18}O$ and values in clouds decrease as the fraction of vapour remaining in the cloud decreases as the cloud front moves inland (Adams, 2004).

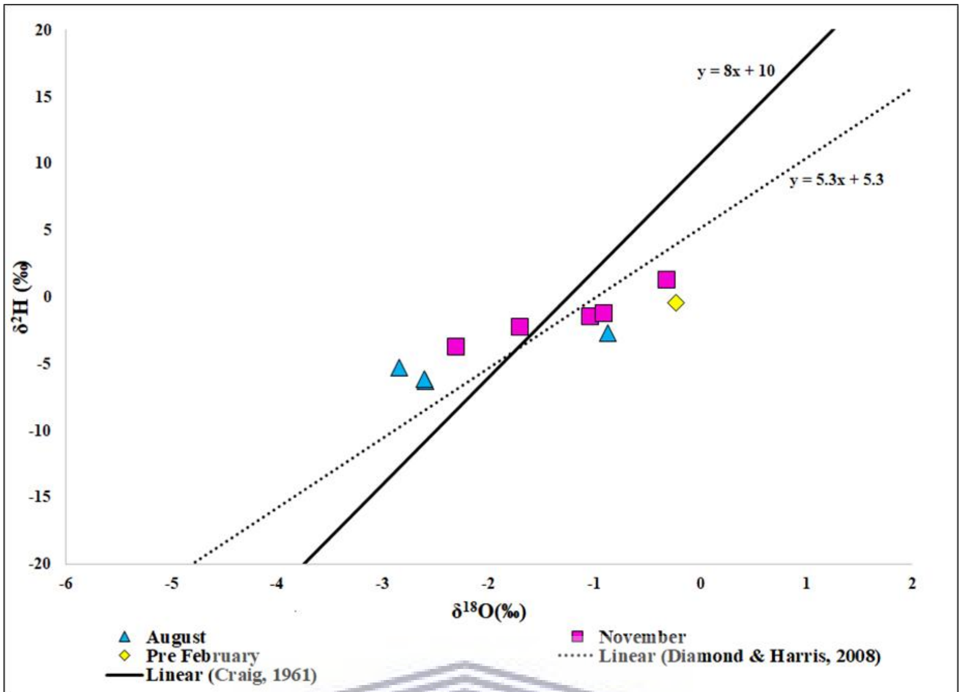


Figure 13: Scatter plot of $\delta^{18}O$‰ and $\delta^{2}H$‰ all rainfall samples collected from August 2017-February 2018

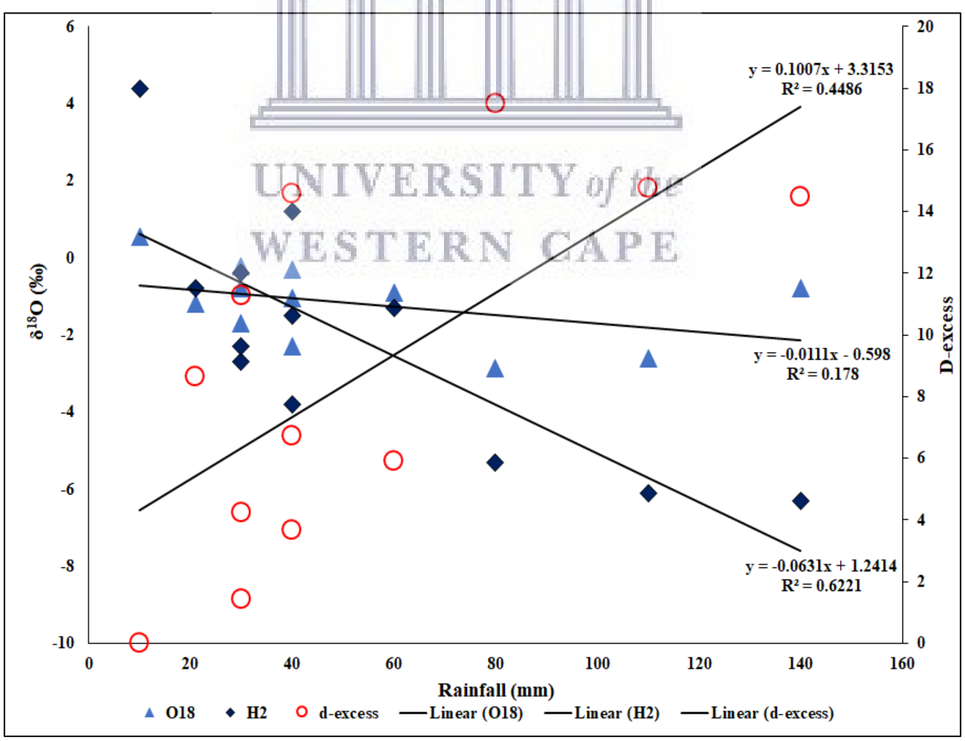


Figure 14: Graphic representation of the relationship between isotopic composition of rainfall $\delta^{18}O$‰ (R^2 = 0.62) and $\delta^{2}H$‰ (R^2 = 0.17) and d-excess (R^2 = 0.44) compared to measured rainfall amount.

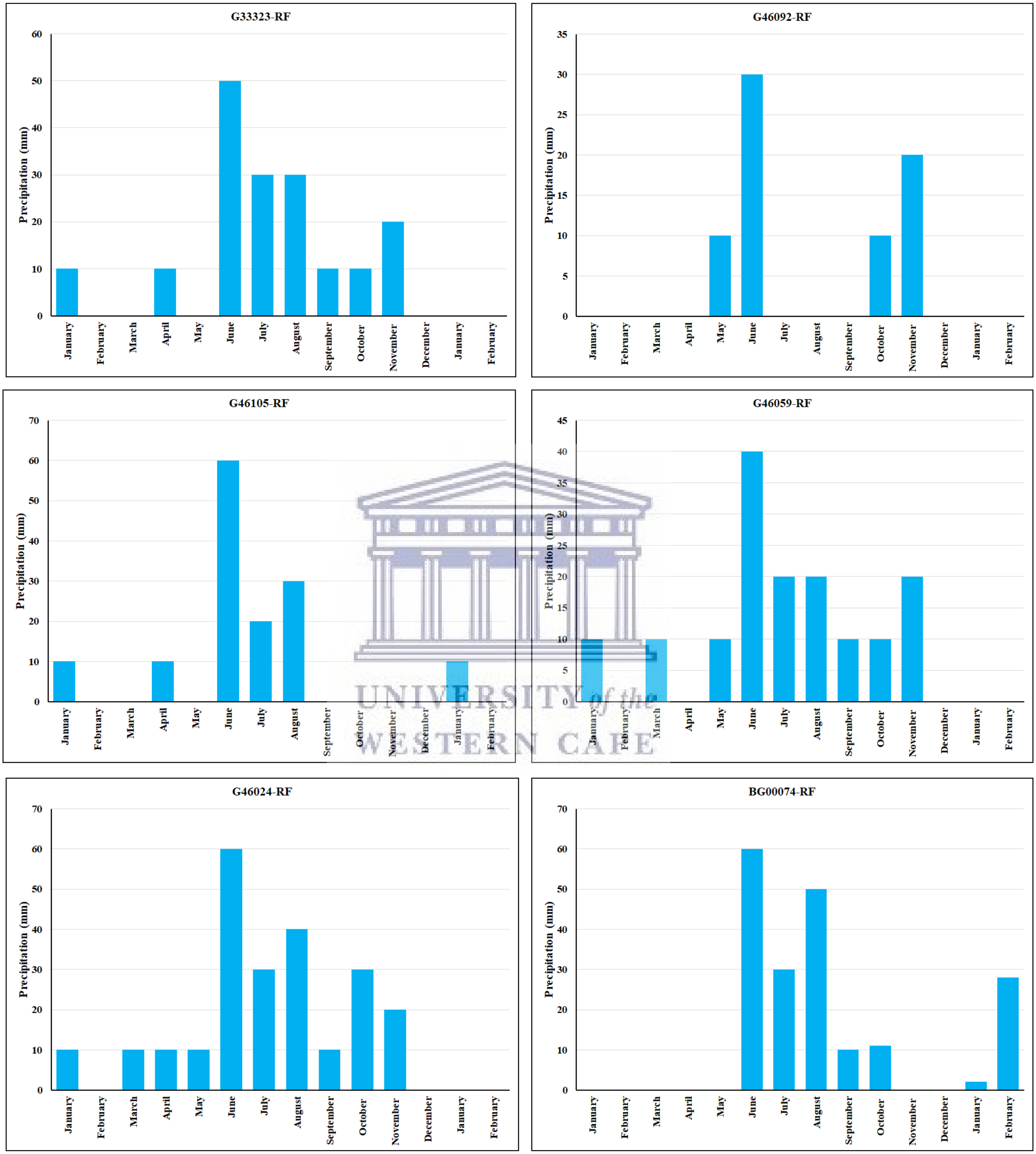


Figure 15: Monthly precipitation at rain gauges in study area (mm/month).

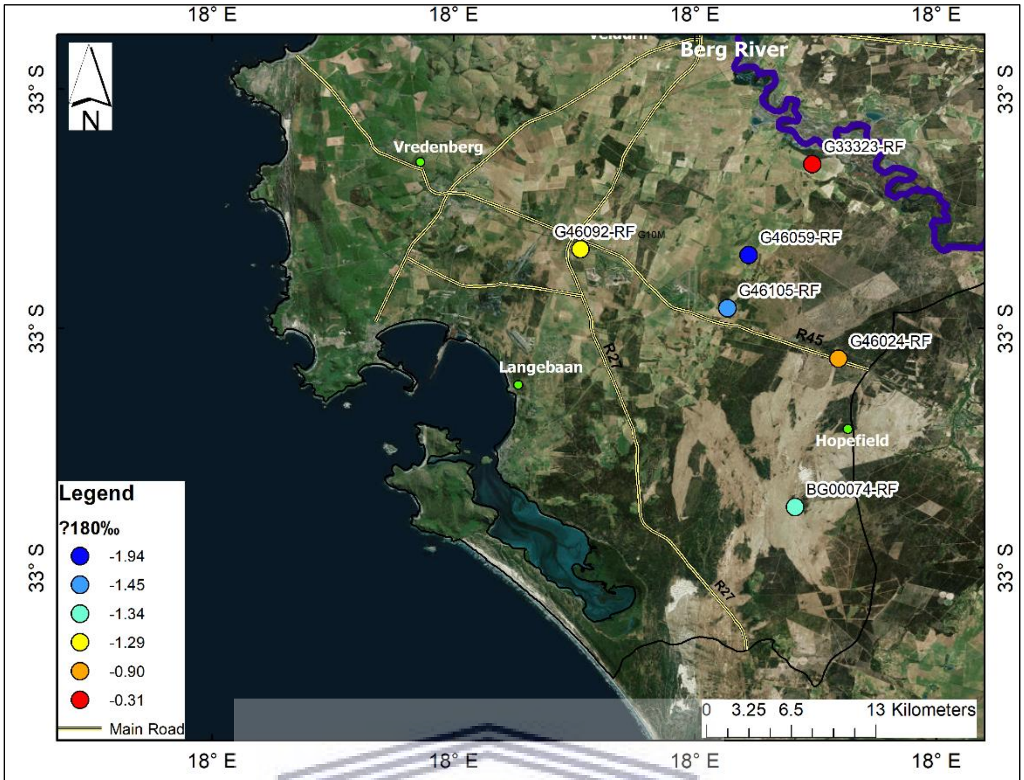


Figure 16: Map illustrating the spatial variation in concentration of $\delta^{18}O$‰ at rain gauges

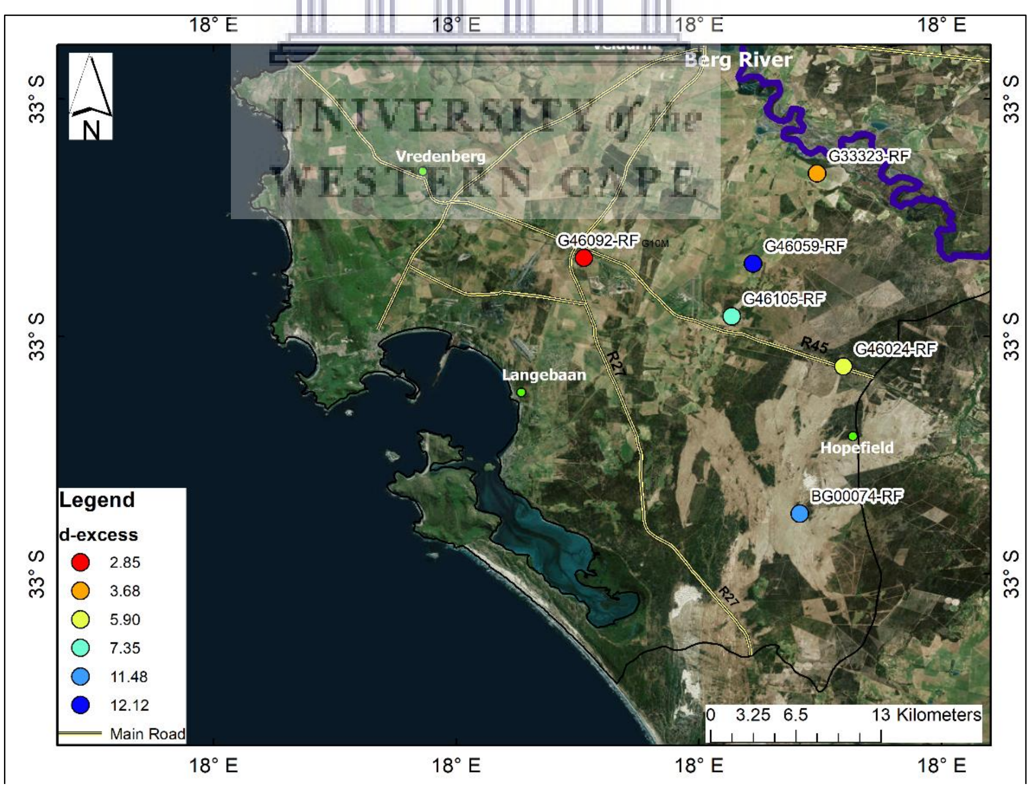


Figure 17: Map illustrating the spatial variation in concentration of d-excess at rain gauges

When comparing δ^{18}O values of rainfall sampled from all rain gauges, δ^{18}O rainfall are observed with increasing rainfall (Figure 18) It can be seen that there are major variations in isotopic composition of rainfall δ^{18}O values as rainfall measurements between 10 to 40mm range from -2.7 to 0.55‰. Rainfall sampled during the winter months for δ^{18}O at BG00074-RF (93mamsl) had measured -0.8‰ and G46092-RF at a lower elevation (43 mamsl) had measured -0.87‰ indicting that elevation is not a major control on rainwater isotopic composition. In November the results show that rainfall sampled at lower elevation are more depleted than rainfall than rainfall sampled at higher elevations. Figure 18 also illustrates that δ^{18}O is more depleted at rain gauge close proximity to the ocean (G46092-RF) at Saldanha than rain gauge furthest inland (G46024-RF) at Hopefield indicating that there are negligible altitude effects.

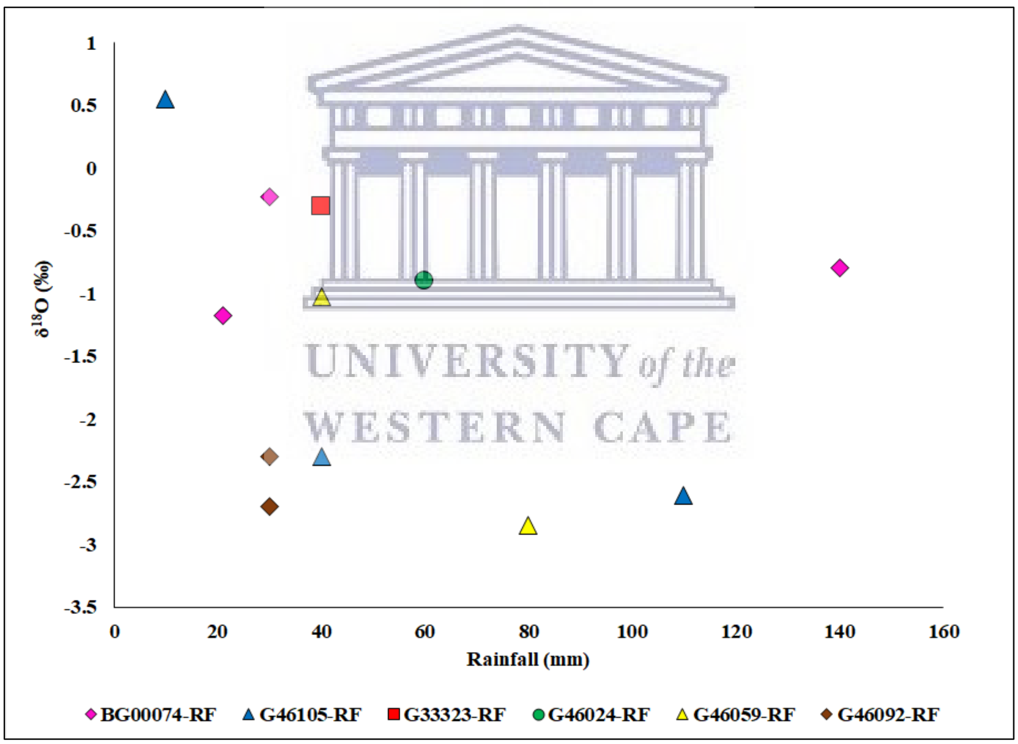


Figure 18: Isotopic composition δ^{18}O of rainwater at all sampled rain gauges with measured rainfall amount.

5.2.2 Groundwater stable isotope results

The standard δ^{18}O and δ^{2}H plot is used to show all groundwater collected for the unconfined, confined and basement aquifer of the West Coast Aquifer System in from May 2017-February

2018 with reference to the GMWL (Craig, 1961) and the LMWL developed by Craig and Harris in 2010. An evaporation line is included in the plot which represents the line of best of best fit through the groundwater samples and is validated by an r-square value. The results of the groundwater analysis will be presented based on the unconfined and the confined aquifer units.

5.2.2.1 Unconfined aquifer

Figure 19 shows the plot of δ^2H against $\delta^{18}O$ for the groundwater sampled from the regional unconfined aquifer in May 2017 to February 2018. The groundwater $\delta^{18}O$ values range from -4.3 1‰ to -2.44‰ with a mean of -3.47‰ and a standard deviation of 0.41‰. The groundwater δ^2H ranges from -18.3 to -3.38‰ with a mean of -15.50‰ and a standard deviation of 2.38‰ as is illustrated in table 5. The groundwater plots distinctly below the rainwater samples and between the GMWL and LMWL during the same sampling period. The groundwater isotope values when plotted define a regression line $\delta^2H = 0.7686\ \delta^{18}O - 13.172$ with a slope value of 0.76. The groundwater shows a weak evaporation trend of (r= 0.0448) and is almost perpendicular to the GWML and LMWL. The mean d-excess obtained by groundwater of the UAU of the WCAS during this study was 12.27 ‰ with a range of 3.32‰ -18.08‰.

Table 5: Statistical summary of stable isotopes of groundwater in the unconfined aquifer

	$\delta^{18}O$‰	δ^2H‰	d-excess
Min	-4.31	-18.3	3.32
Max	-2.44	-3.38	18.08
Mean	-3.47	-15.50	12.27
Standard Deviation	0.41	2.38	4.47

The seasonal variations in groundwater δ-values for the unconfined aquifer are depicted in Figure 19. Seasonal variation in isotopic composition is observed in groundwater of the unconfined aquifer. The degree of temporal variation is different between boreholes (Figure 20). The results for groundwater sampled in May 2017 prior to the onset of the rainy season shows that G46028 is the most enriched (δ^2H= -14.5; $\delta^{18}O$= -2.7) and G46092 (δ^2H = -3.38; $\delta^{18}O$ = -2.44) plots in the same region as rainfall samples Groundwater sampled in August 2017 during the winter rainfall season shows a shift in isotopes towards from the GMWL in May, towards the LMWL in August which is expected. Most of the groundwater sampled in November (pre-dry/post-wet season) shows a general shift in isotopic composition from LMWL towards the GMWL. G46092 shows groundwater that is most enriched during November 2017 (δ^2H=-16.3; δ^{18}O=-3.29) and shifts below the GMWL. Groundwater sampled during the dry season (February 2018) shows groundwater which is depleted and enriched. G46060 is the most enriched sample and plots below the GMWL (2017 (δ^2H=-17.0‰; δ^{18}O=-2.54‰) and the most depleted is G33502C which plots on the LMWL above the GMWL with δ^2H=-17.6‰ and δ^{18}O= -4.31‰.

The seasonal variation can be seen in the δ^{18}O values figure 19 and for the unconfined aquifer. The time series revealed that groundwater δ^{18}O values of the unconfined aquifer was the most depleted at G33502C (figure 20). The spatial distribution of groundwater δ^{18}O values illustrates that groundwater for the UAU is most depleted in the south and becomes increasing heavy in heavy isotopes towards the Berg River (figure 21). It is also interesting to note that the groundwater ^{18}O values at topographically lower region(G46060) is not significantly different at boreholes sampled at higher elevation(G46024).

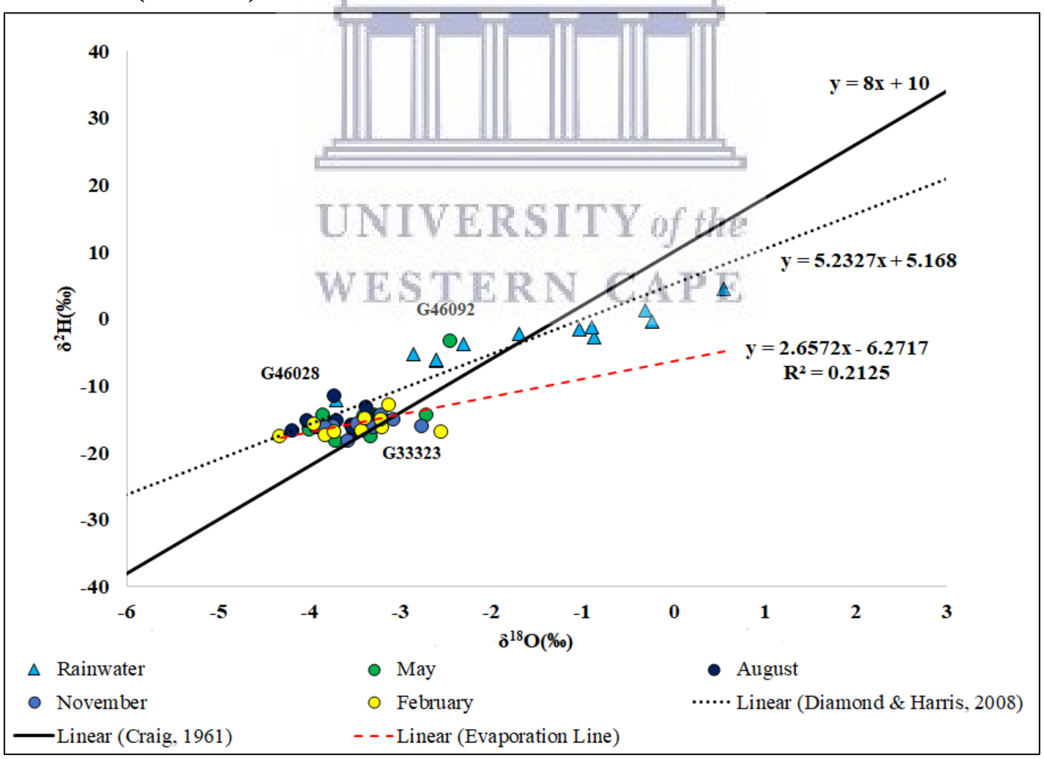


Figure 19: Plot of δ^2H and δ^{18}O for groundwater from the unconfined aquifer and rainwater for the WCAS

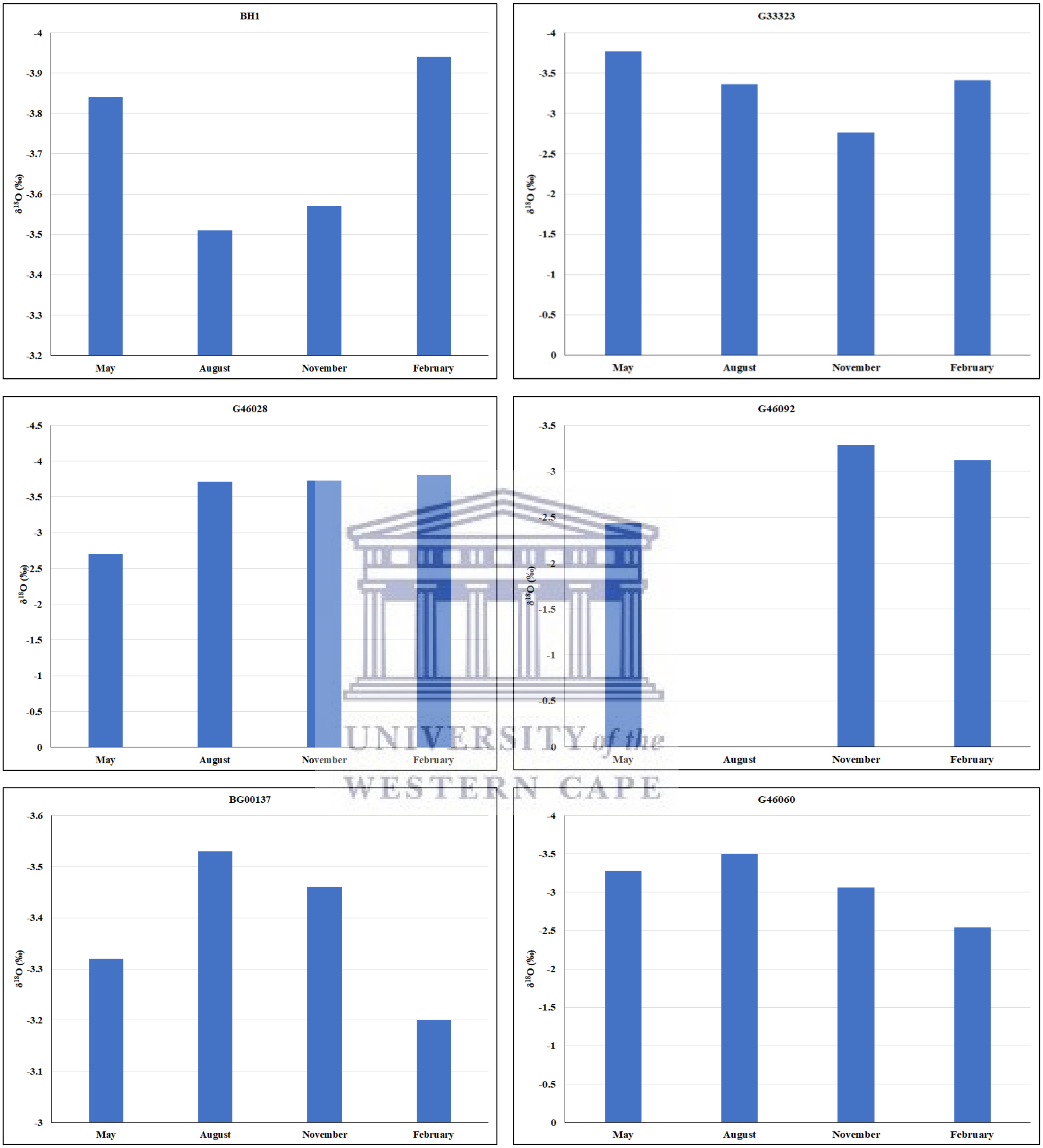


Figure 20: Graphical representation of the temporal variation of $\delta^{18}O$ and $\delta^{2}H$ concentrations at different boreholes that penetrate the unconfined UAU from May 2017 to February 2018.

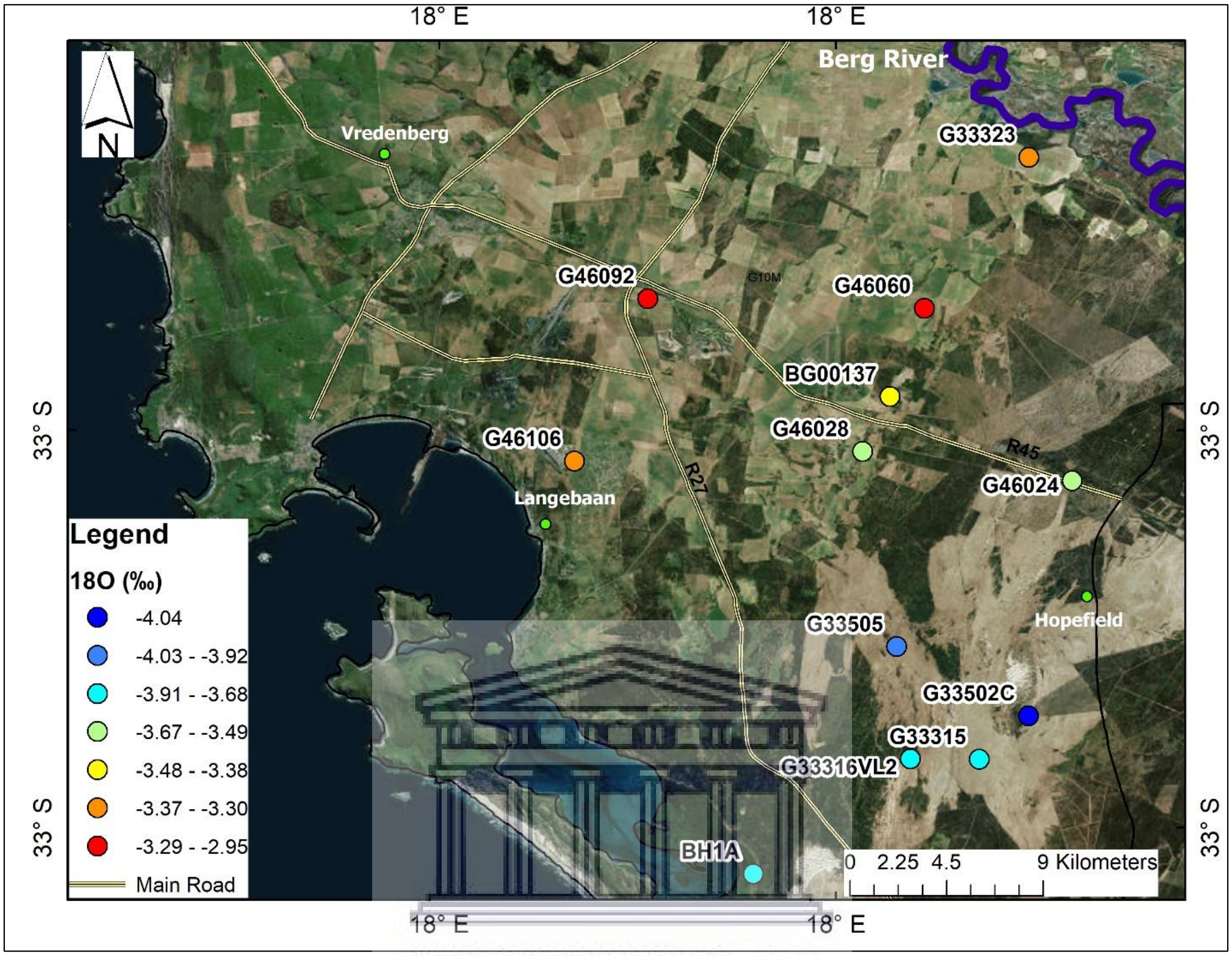


Figure 21: Spatial distribution of δ^{18}O‰ of groundwater for the unconfined aquifer

5.2.2.2 Confined Langebaan Road Aquifer Unit (LRAU) and Elandsfontein Aquifer Unit (EAU) and Bedrock Aquifer

Figure 22 shows the plot of δ^2H and δ^{18}O for groundwater sampled from the confined aquifers lower aquifer units and the bedrock aquifers in May 2017 through February 2018. Table 6 presents the results in a statistical format of the all samples of the LAU. The LRAU groundwater δ^{18}O values range from -4.06‰ to -3.24‰ with a mean of -3.69‰ and a standard deviation of 0.23‰. The LRAU groundwater δ^2H values range from -18.8 to -13.9‰ with a mean of -16.01‰ and a standard deviation of 1.26‰. The mean d-excess obtained for groundwater of the LRAU of the WCAS during this study was 13.45‰ with a range from 9.52‰-16.42‰. The EAU groundwater δ^{18}O values range from -4.12 to 0.65‰ with a mean of -2.54‰ and a standard deviation of 1.94‰. The EAU groundwater δ^2H values range from -18.7 to 6.8‰ with a mean of -10.09‰ and a standard deviation of 9.79‰. The mean d-excess obtained from the EAU was 10.78‰ and ranged from -1.3‰ - 16.64‰. Groundwater sampled from Malmesbury Shale basement from May 2017 and February 2018 had $\delta^{18}O$ values range from -4.34 to -2.45‰ with a mean of -3.64‰ and a standard deviation of 0.54‰ and $\delta^{2}H$ values range from -16.6‰ to -14.7‰ with a mean of -15.85‰ and a standard deviation of 0.54‰. Groundwater sampled from Malmesbury Shale basement that underlies the EAU in August 2017 and February 2018 had $\delta^{18}O$ values range from –4.34 to -3.68‰ with a mean of -4.01‰ and a standard deviation of 0.47‰ and $\delta^{2}H$ values range from -17.20 to -14.90‰ with a mean of -16.05‰ and a standard deviation of 1.63‰. The mean d-excess obtained for groundwater of the bedrock aquifer of the WCAS was 13.98‰ with a range of 4.9‰ – 17.52‰

Table 6: Statistical summary of stable isotopes of groundwater in the confined aquifer in the West Coast.

	$\delta^{18}O$‰	$\delta^{2}H$‰	d-excess
Min	-4.34	-18.8	-1.30
Max	0.65	6.8	17.52
Mean	-3.71	-13.5	12.25
Standard Deviation	1.32	6.7	4.53

The seasonal variations in groundwater δ-values for the confined aquifer are depicted in Figure 22. There are seasonal correlations between individual boreholes of the confined. Temporal variation exists between groundwater at individual boreholes and temporal fluctuations in $\delta^{18}O$ at each borehole is observed (Figure 23). The regional distribution of groundwater $\delta^{18}O$ is shown in figure 24. In May, of all groundwater sampled, the bedrock aquifer (G46105) is the most enriched in heavy isotopes for the WCAS ($\delta^{2}H$= -14.7; $\delta^{18}O$= -2.45) and plots furthest below the GMWL (figure 22). During the winter rainfall season, a drastic shift in isotopic composition between groundwater sampled in May and August from the bedrock aquifer shifts from the GMWL towards to LMWL is observed, which was not expected due to longer travel assumed longer groundwater flow paths. All groundwater sampled in November shifts towards the GMWL from the LMWL which is indicative of groundwater that experiences some evaporation effects before infiltration.

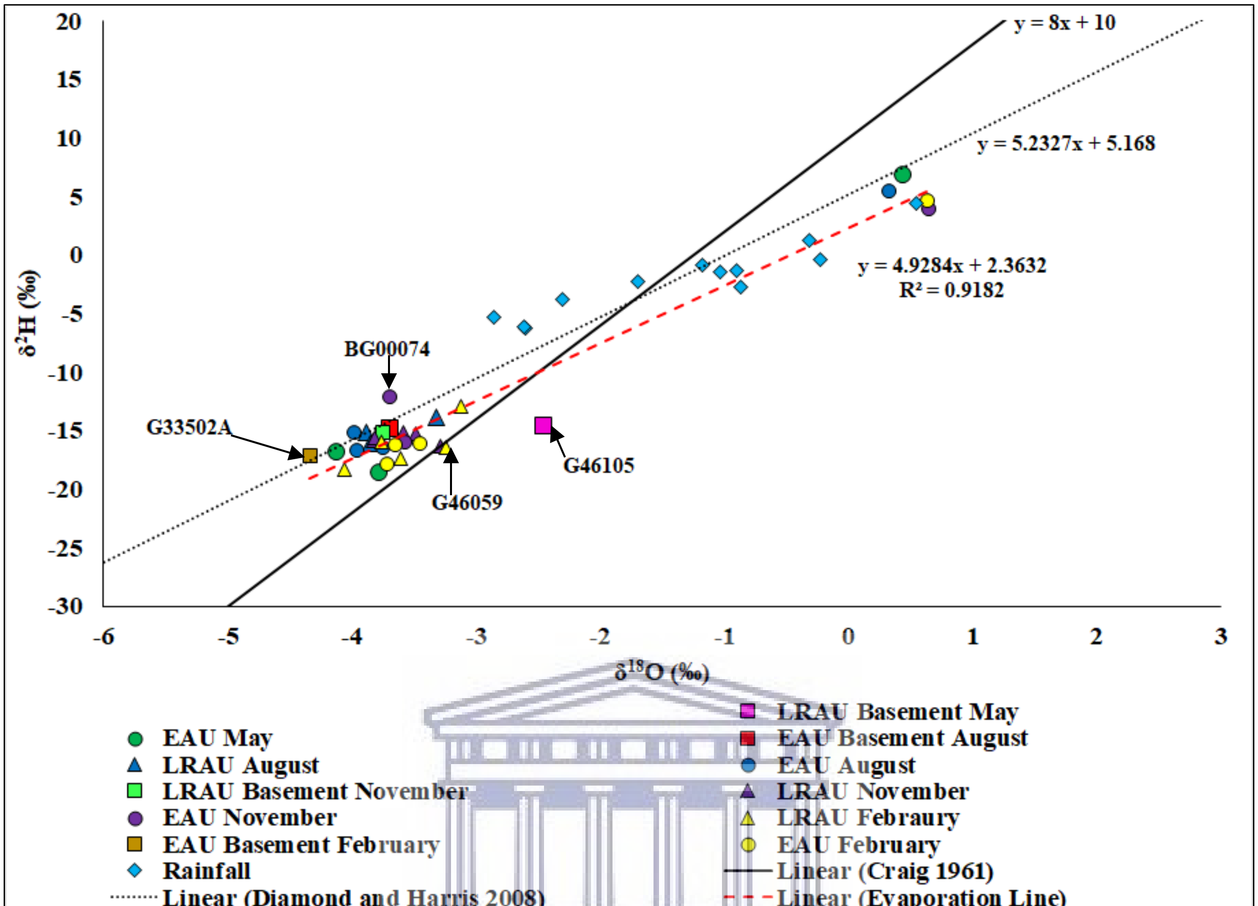
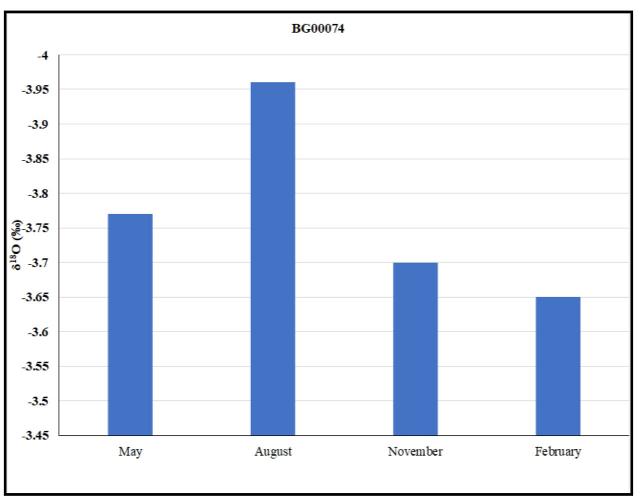
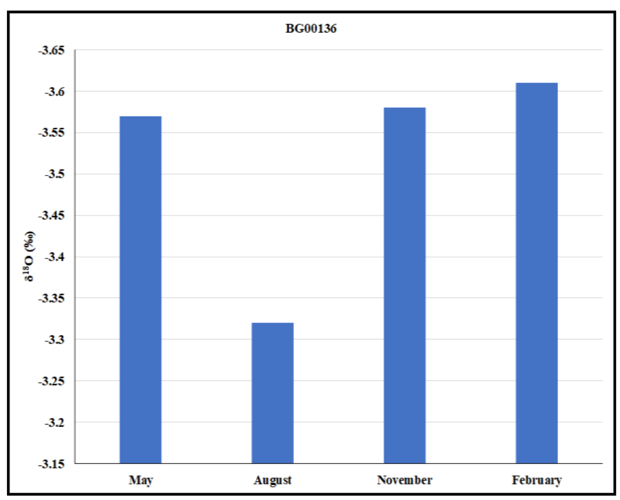


Figure 22: Plot of δ^2H and $\delta^{18}O$ for groundwater from the confined aquifer and rainwater





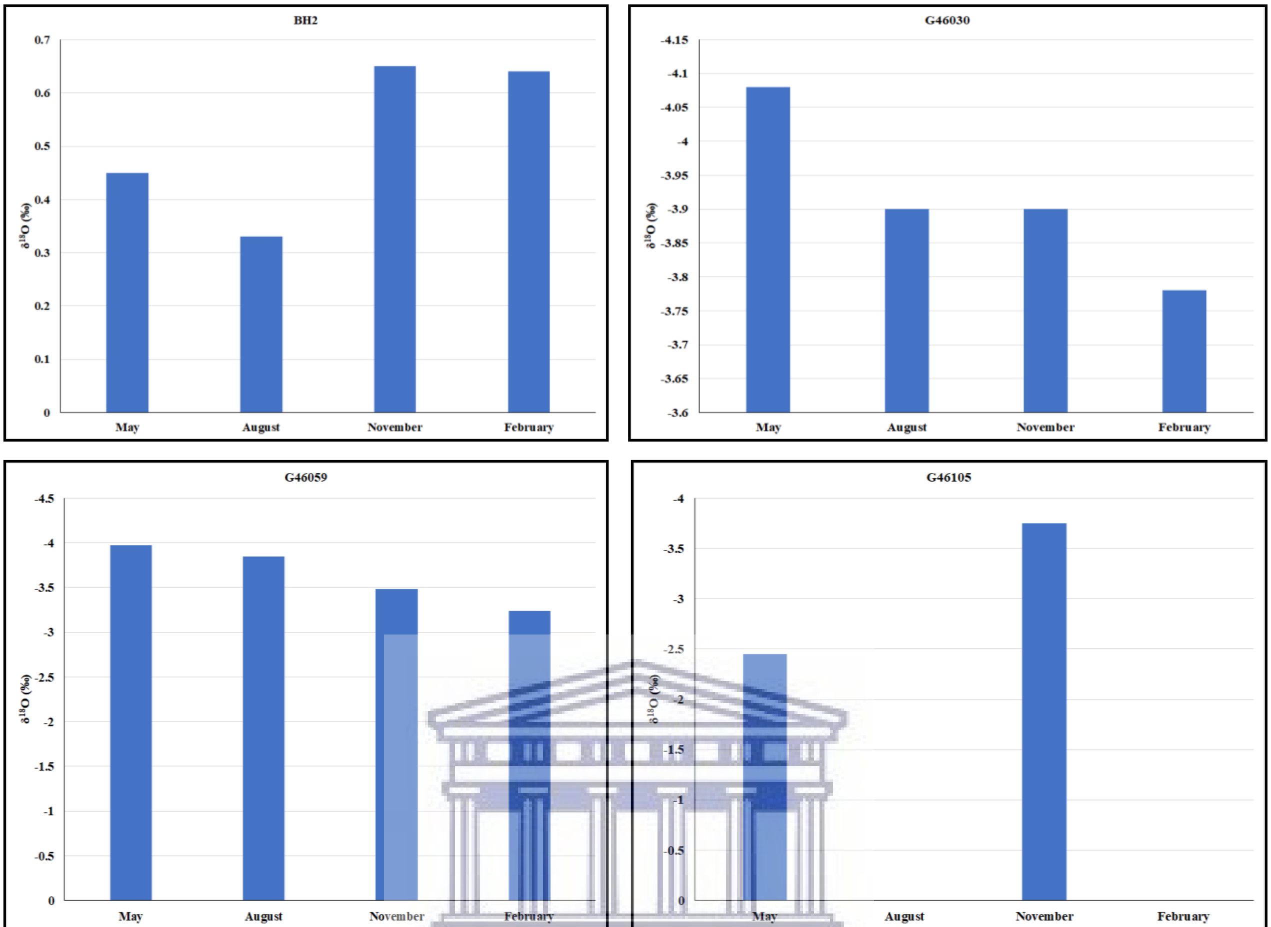


Figure 23: Graphical representation of the temporal variation of $\delta^{18}O$ concentrations at different boreholes that penetrate the LAU of the WCAS from May 2017 to February 2018.

Groundwater sampled from the bedrock aquifer at the Langebaan Road Wellfield (G46105) plots above the GMWL and is depleted in heavy isotopes (δ^2H=-15.1; $\delta^{18}O$=-3.75), compared to May when groundwater the same borehole plotted below the GMWL. Groundwater sampled during the dry season (February 2018) shows groundwater becomes and enriched in heavy isotopes and plots closer to the GMWL which is expected. G46059 is the most enriched sample and is the only sample from confined aquifer which plots below the GMWL (δ^2H=-16.4‰; $\delta^{18}O$=-3.24‰) during the hot summer month of February. Figure 20 illustrates that groundwater $\delta^{18}O$‰ sampled at boreholes that penetrate the LRAU (G46059), EAU (BG00074) and bedrock aquifer (G46030) becomes more enriched in heavy isotopes during the data collection which is indicative of groundwater that is experiencing persistent evaporation effects prior to infiltration.

A strong evaporation trend illustrated the evaporation line (r = 0.91) is not influenced by the isotopic composition of BH2 but representative of the groundwater stable isotope concentration of the LAU (Figure 22). Groundwater in the confined aquifer illustrates groundwater of two different systems; all of the groundwater for the confined aquifer plots below the rainfall samples between the GMWL and LMWL and tends more negative on the graph, and the groundwater at BH2 that plots above the rainfall samples and tends more positive on the graph in comparison with all other groundwater of the EAU and LRAU. The groundwater in unconfined, confined LRAU and EAU and the basement aquifer all range in similar δ^2H and $\delta^{18}O$ values, except groundwater at BH2. The groundwater in the LRAU is slightly more enriched in heavy isotopes than groundwater of the EAU.

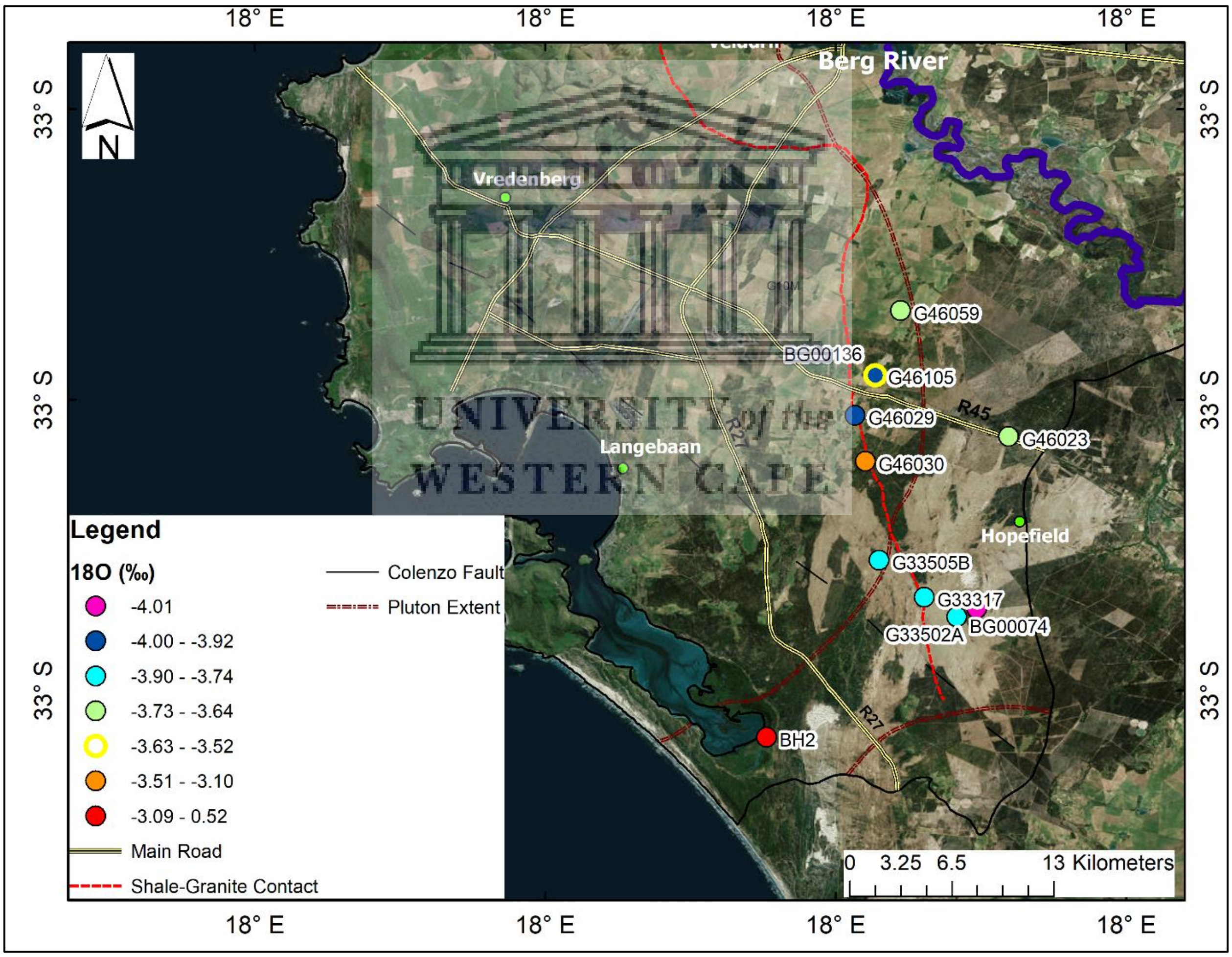


Figure 24: Spatial distribution of ^{18}O in groundwater of the LAU and bedrock aquifer

5.2.3 Surface water

Figure 25 shows the plot of stable isotope composition of the Berg River and the Geelbek Lagoon collected from May 2017 to February 2018 with all rain and groundwater samples. The $\delta^{18}O$‰ of three samples collected in the lower reach of the Berg River ranged from -0.34‰ – 4.98‰ with a mean of 2.86‰ and a standard deviation of 2.3‰. The $\delta^{2}H$‰ ranged from 4.7‰ – 23.1‰ with a mean of 16.23‰ and a standard deviation of 8.2‰. Two samples were collected for stable isotope analysis from the Langebaan lagoon at the Geelbek Nature Reserve in August 2017 and February 2018. The $\delta^{18}O$‰ ranged from 0.45‰ – 2.05‰ with a mean of 1.25‰ and a standard deviation of 0.8‰, the $\delta^{2}H$‰ ranged from 9.2‰-11.9‰ with a mean of 10.55 ad a standard deviation of 1.35‰.

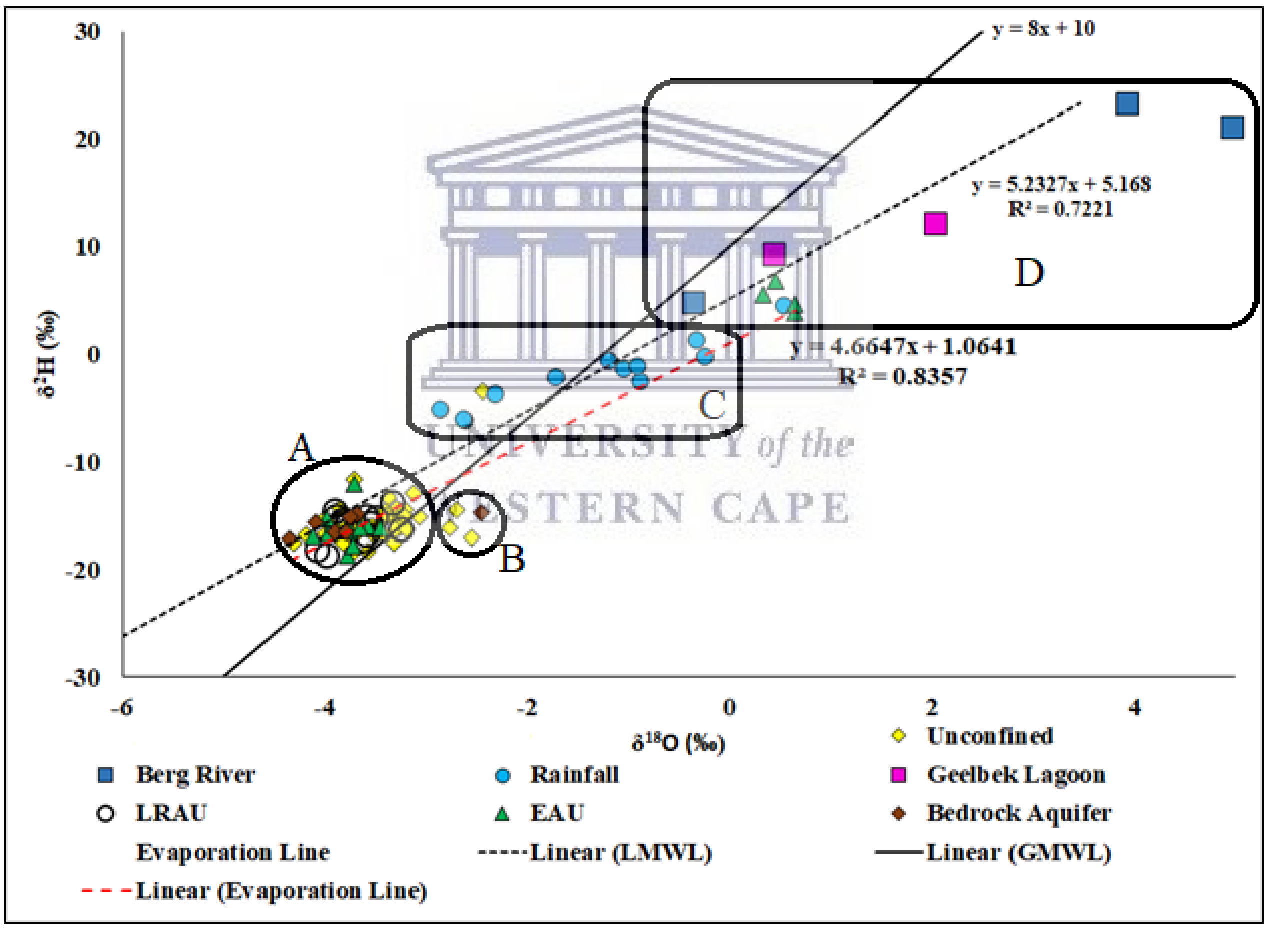


Figure 25: Stable isotope composition of all Rain, surface and groundwater samples collected in the West Coast.

The isotopic composition of the Berg River become more depleted in heavy isotopes during the raining winter months (June-August) compared to the dry summer months (May and February). Rainfall δ^2H‰ and δ^{18}O‰ values are -2.08‰ and -1.34‰ similar to that of δ^2H‰ and δ^{18}O‰ of water in Berg River in winter 4.7‰ and-0.34‰. Since the Berg River plots close to the rainfall samples during winter rainfall season suggests that rainfall that is depleted in heavy isotopes contributes to streamflow and that flow derived from upstream tributaries and runoff generated in the study area are the reasons for the seasonal shift in isotopic composition in the wet months compared to the dry months. The Berg River δ^2H‰ and δ^{18}O‰ values subsequently become enriched with heavy isotopes due to decrease in relative humidity, increase in temperature and evaporation effects.

The groundwater δ^2H‰ and δ^{18}O‰ values are -14.67‰ and -3.37‰ which are distinctly different from the rainfall and Berg River values, which suggests that surface water is not source of recharge to groundwater in the WCAS. The average δ^2H‰ and δ^{18}O‰ values of groundwater at BH2 located close to the Geelbek Lagoon are 5.4‰ and 0.48‰ and at the lagoon was 10.55‰ and 1.25‰ respectively, which suggests that groundwater and lagoon are in hydraulic connection. The isotopic composition of the Geelbek Lagoon shifts from being depleted in heavy isotopes in winter to being enriched in heavy isotopes in summer months due to tidal influences and increase in relative humidity.

5.3 Radioactive environmental tracers (^{3}H and ^{14}C)

5.3.1 Tritium

Figure 26 illustrates the results of groundwater tritium activities which is shown as a function of δ^{18}O‰ as these parameters were used as proxies for groundwater recharge. Rainwater that was sampled once for tritium analysis resulted in 1.4 T.U. The groundwater ^{3}H activities for the unconfined aquifer ranged from 0.0 T. U - 1.2T. U with a mean of 0.5T.U and a standard deviation of 0.37T.U (Table 7). The results exhibit that tritium activity of some of the shallow boreholes of the unconfined aquifer were below detection limit, which was not expected due to its direct exposure to rainfall. The LRAU groundwater ^{3}H activities ranged from 0.0T.U-0.8T.U with a mean of 0.2T.U and a standard deviation of 0.33 T.U. The groundwater activity for the EAU had the smallest range from 0.0-0.3T.U with a mean activity of 0.1 T.U and a standard deviation of 0.14T.U. For the two tritium samples taken from the bedrock aquifer, ^{3}H activity was recorded as 0.2 and 0.7T.U with mean of 0.5T.U and a standard deviation of 0.35T.U. The elevated tritium activity for groundwater in the deep aquifers of the LRAU and the bedrock aquifer was not expected. The spatial distribution of groundwater tritium activities is illustrated is illustrated for the unconfined (figure 27) and confined aquifer (figure 28). For all groundwater that sampled from the WCAS which was sampled during the wet winter month of August (n=21), ^{3}H activities was the highest for the unconfined aquifer followed by the LRAU and bedrock aquifers which has activities of 1.2(G46060), 0.8(46029) and 0.7(G46105) T.U respectively. Groundwater tritium activities shows good positive correlation with stable isotope data, as deep groundwater which experienced enriched isotopic signatures had elevated ^{3}H activities. The spatial distribution illustrates that for the unconfined aquifer tritium activity is highest close geological features such as the shale-granite contact and Colenso Fault, are deformations in the basement. The ^{3}H results for the LAU are generally below detection limit and there is no correlation with topography in the region. 3H activity is generally highest for the UAU in the north and decreases southwards. The LRAU exhibits greater tritium activity than the EAU. Tritium activity does not correlate well with water table elevation. ^{3}H activity is low in the region where the water table for the LAU and UAU is the highest close to topographically high area in Hopefield. Comparatively, groundwater ^{3}H is higher in topographically lower regions towards the west.

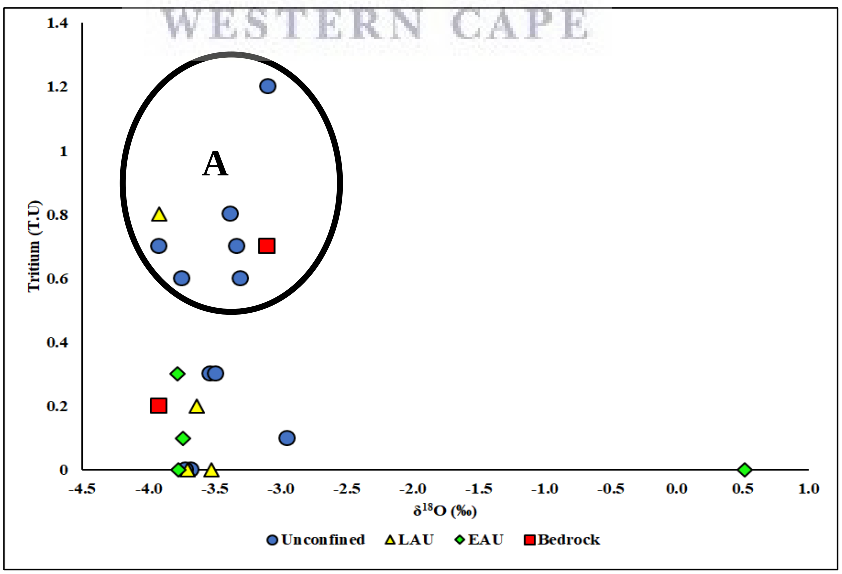


Figure 26: Plot of ^{3}H and δ^{18}O‰ illustrating tritium activity for the WCAS. (A) Illustrates most recently recharged groundwater

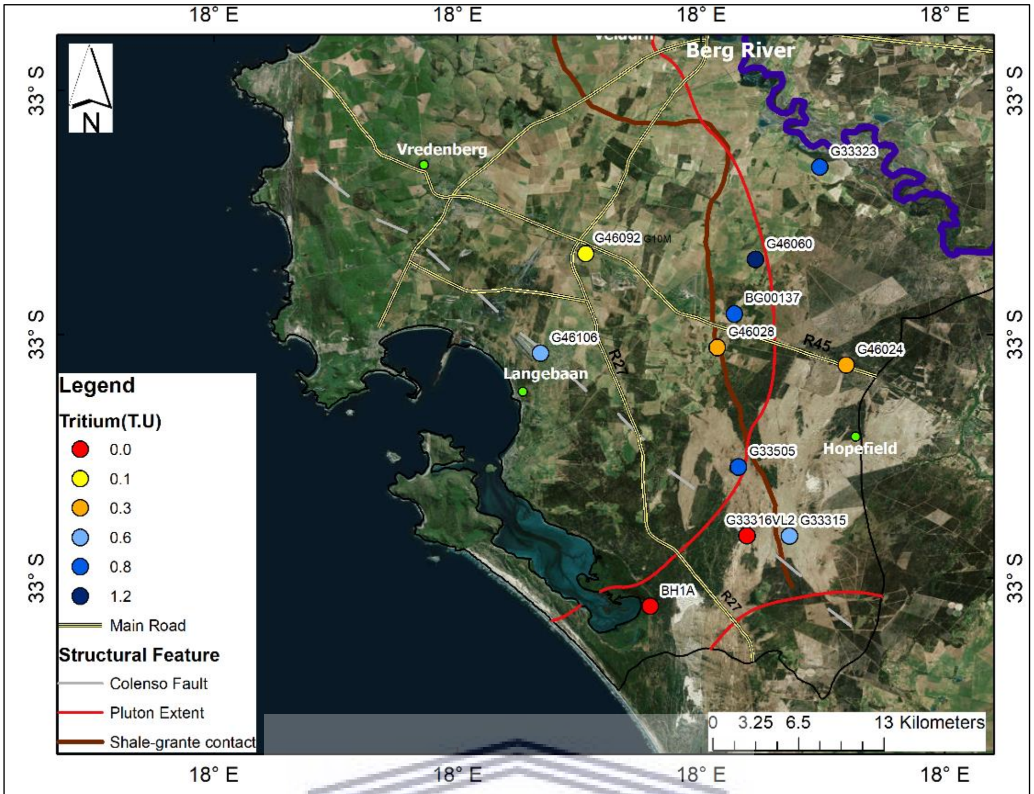


Figure 27: Spatial distribution of groundwater tritium (T.U) for the unconfined aquifer

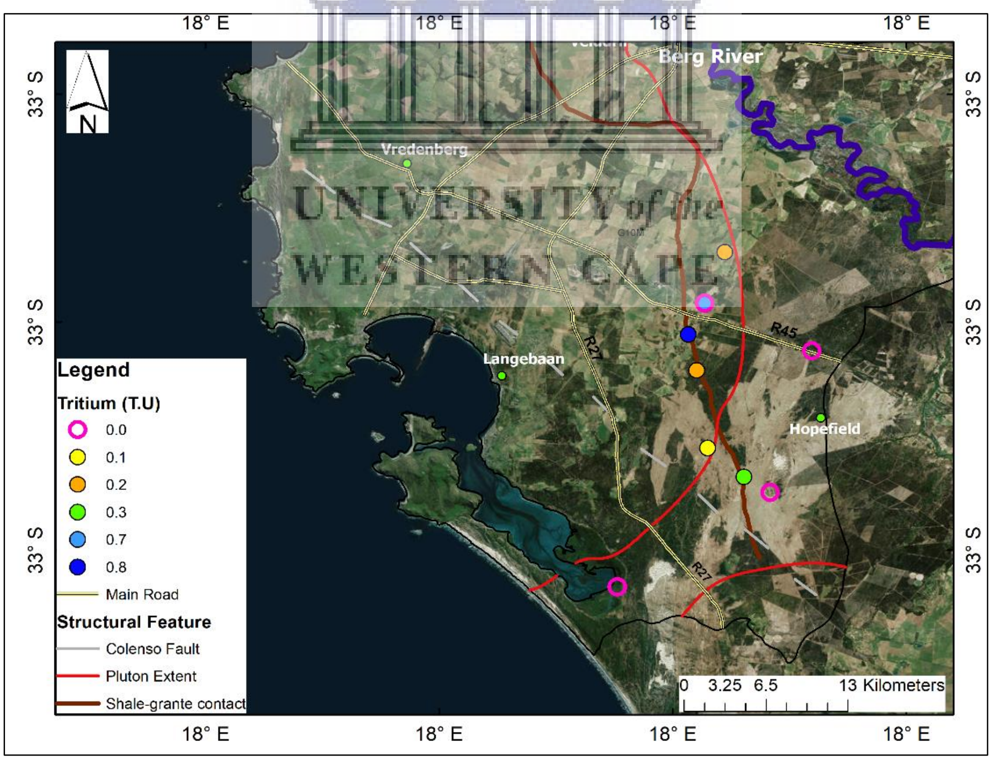


Figure 28: Spatial distribution of groundwater tritium (T.U) for the confined aquifer

5.4.2 Radiocarbon

Figure 29 illustrates results of groundwater radiocarbon activities as function of $\delta^{18}O$‰. Groundwater radiocarbon was analyzed from nine boreholes that penetrate into all hydrogeological units of the WCAS; four from the unconfined aquifer, one from the LRAU, three from the EAU and one from the bedrock aquifer. The statistical summary of $\delta^{18}O$ and $\delta^{2}H$ values of groundwater ^{14}C content is presented in Table 7.The groundwater sampled from the unconfined aquifer contain the highest ^{14}C contents and ranged between 22.9-61.2 pMC with mean of 40pmC. The only groundwater sample from the LRAU had ^{14}C content of 17.6pMC. Groundwater ^{14}C contents of the EAU of 3.2 and 4.9pmC upgradient and eastwards and downgradient and eastwards of the aquifer, ^{14}C content was 59.1pMC at the Geelbek Lagoon (BH2). The spatial distribution of ^{14}C is shown in figure 30 (unconfined aquifer) and figure 31(confined aquifer).The highest groundwater ^{14}C content was sampled from boreholes that are in close proximity to the coast (G46106 and BH2). Figure 29 illustrates that ^{14}C contents correlated the better than other environmental isotopes with aquifer depth as the pMC contents in the UAU were higher than the LRAU, EAU and bedrock aquifer respectively, which was expected. The southern paleochannel EAU has a lower ^{14}C activity than the LRAU which has a ^{14}C activity that is in close range to the pMC content in the UAU. The high ^{14}C activity of groundwater at Geelbek corresponds to tritium activity that is below detection limits and highly enriched in heavy isotopes.

Table 7: Results of radiogenic isotopes

	^{3}H (T.U)	^{14}C (pMC)
n	21	9
Min	0.0	0.0
Max	1.2	61.2
Mean	0.4	27.56
Standard Deviation	0.36	23.45

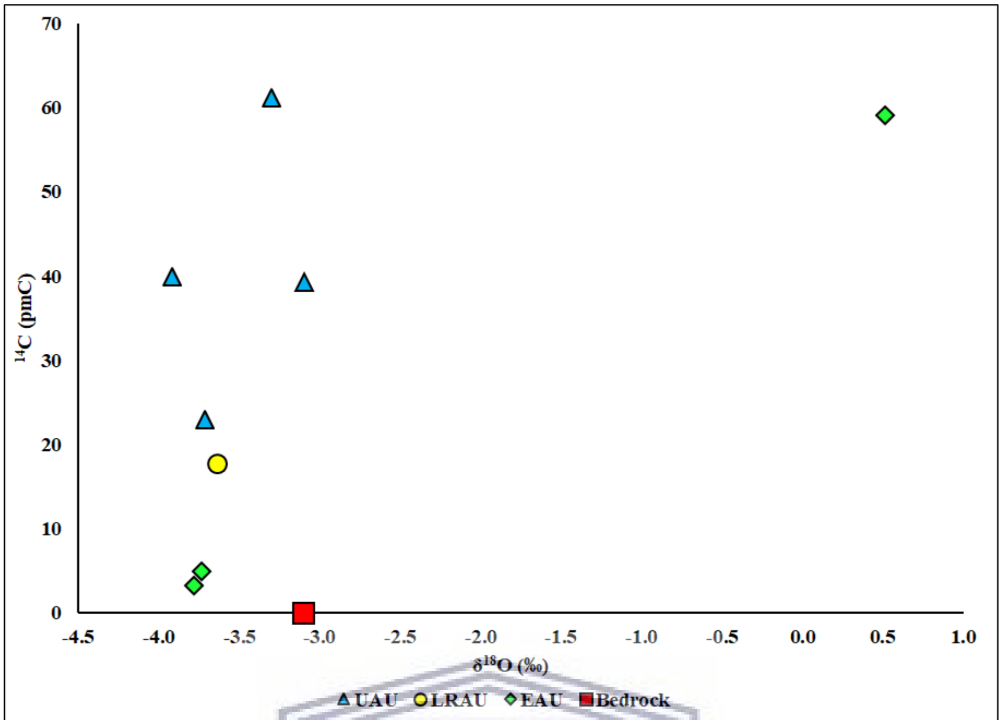


Figure 29: Plot of ^{14}C (pMC) and δ18O‰ illustrating groundwater age

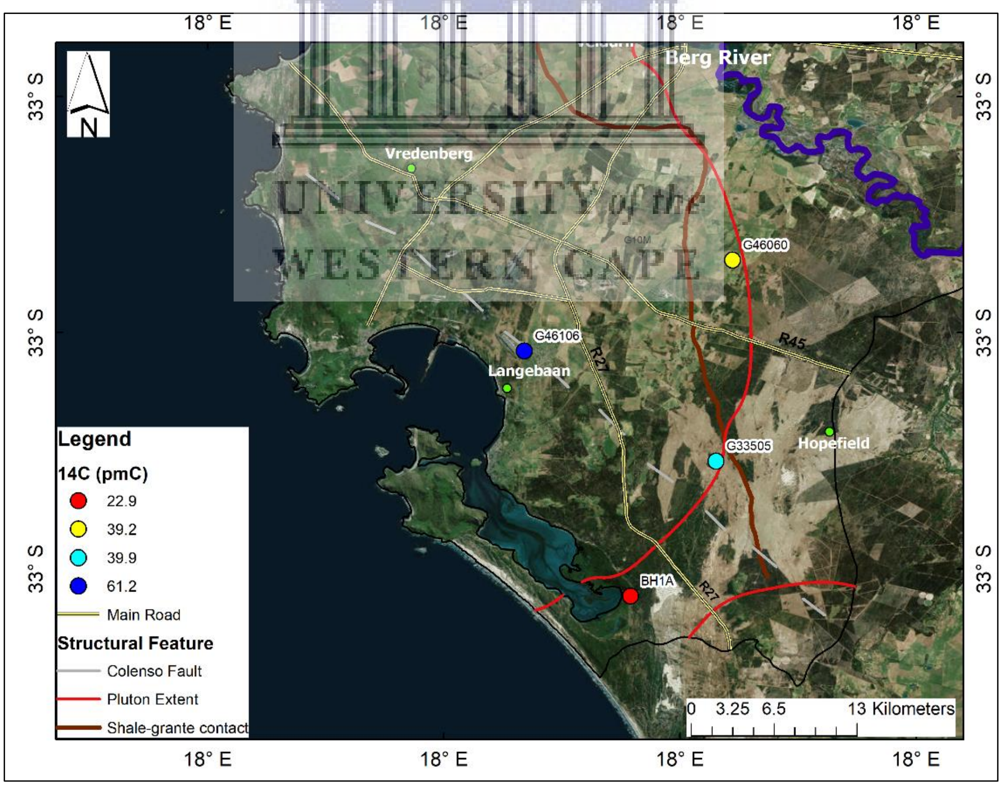


Figure 30: Spatial distribution of groundwater ^{14}C (pMC) for the unconfined aquifer

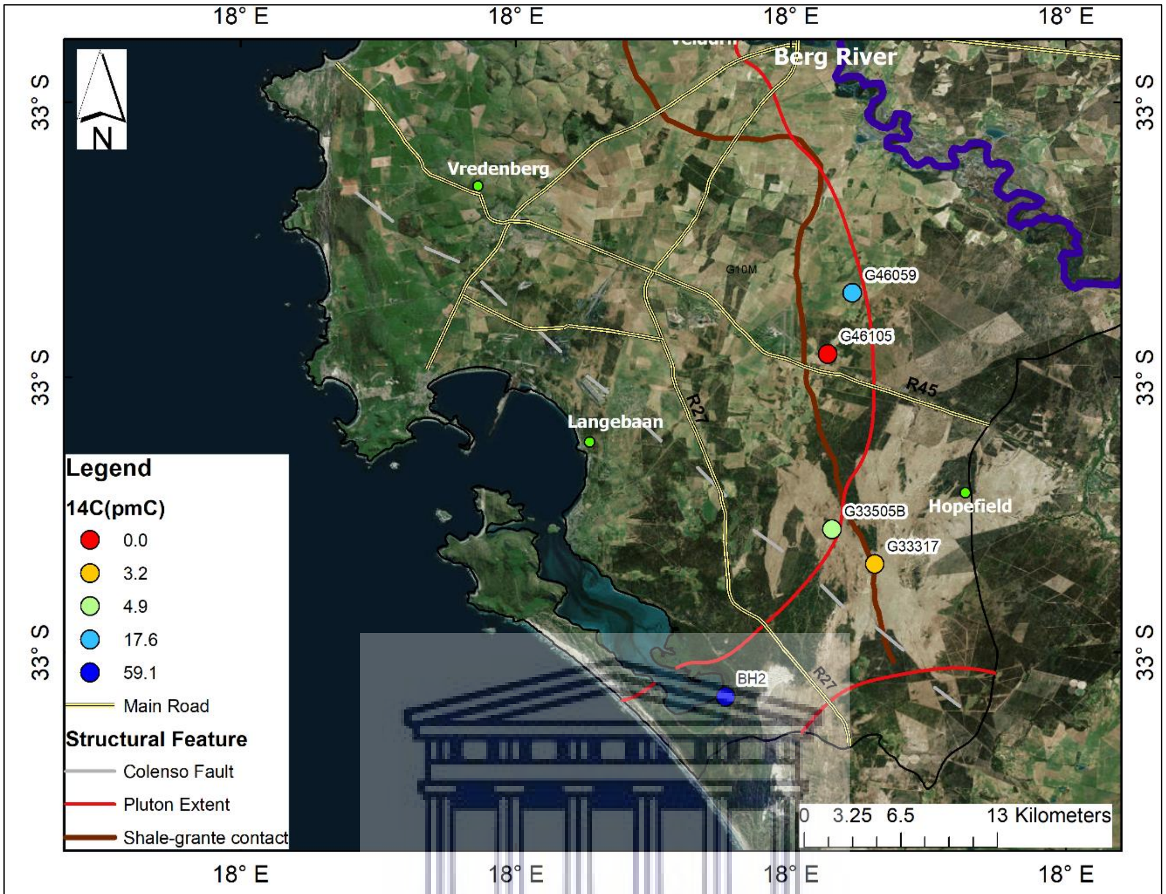


Figure 31: Spatial distribution of groundwater ^{14}C (pMC) for the confined aquifer.

5.5 Discussion

5.5.1 Rainwater

The study area receives winter rainfall, with cold fronts arriving from a westerly direction from the Atlantic Ocean. The observed rainwater stable isotope composition in the West Coast is a consequence of seasonal effects. As temperature and relative humidity increases and the frequency of rainfall events decreases in the West Coast, there is slight evaporation of rainwater samples which results in subsequent enrichment of rainwater during descent. During the winter rainfall month of August their stable isotope composition displays the continental effect where there is general increase trend of -δ values away from the coast and further inland. Depletion of heavy isotopes in rainwater is a consequence of the cooler temperature that reduces evaporation and higher relative humidity experienced at the coast (Diamond, 2014; Clarke & Fritz, 1997). From the analysis $\delta^{18}O$‰ data and $\delta^{2}H$‰ data rainwater sampled at 89mamsl is more enriched than rainwater sampled at 10mamsl which illustrates that the altitude effect has minimal influence on the isotopic composition of rainwater. The shift of depleted rainwater to enriched rainwater signature is indicative of water being subject to evaporation (Bugan et al, 2012). However, the rainwater plots near the LMWL which is indicative that rainwater has experienced minimal evaporation.

The d-excess values for the 6 rain gauges ranges from 1.44 to 17.50‰ with an average of 9.39‰. The range is slightly lower than the range for rainfall isotopic composition by Diamond 2014 which were 5.8 to 22.7‰ and an average is slightly higher 16.0‰. The range is similar to d-excess rainfall values for Velorenvlei -0.1 to 26.5‰ (Eilers, 2018). D-excess was the lowest at 1.44‰ for rainwater sampled in February at BG00074-RF at the Elandsfontein Nature Reserve and the highest at G46059-RF 17.50‰ in August. There is a general decrease in d-excess values from the winter rainfall, rainfall collected during the onset of and rainfall collected in the dry summer months meaning there is a strong trend with seasonality. The seasonality effect is seen at all rain gauges beside G46092-RF which is the closest to the coast where there is an increase in d-excess values during the winter rainfall and rainfall collected in November 2017. No correlations exist between the continentality factors.

5.5.2 Groundwater

The groundwater $\delta^{18}O$ values for the unconfined aquifer range from -4.31‰ to -2.44‰ and the groundwater $\delta^{2}H$ ranges from -18.3 to -3.38‰ with a noticeably larger range. The groundwater $\delta^{18}O$ values range for the deep aquifer range from -4.34‰ to 0.65‰ and the groundwater $\delta^{2}H$ ranges from -18.8 to 0.65‰ with a noticeably larger range than the unconfined aquifer. The larger range can be attributed to outlier at the southern end at the Geelbek Lagoon (BH2) of the EAU which is not representative of groundwater of the WCAS. Groundwater sampled at this site $\delta^{18}O$ values range from 0.33‰ to 0.65‰ and the groundwater $\delta^{2}H$ ranges from 3.9 to 6.8‰. This demonstrates the deep aquifer accounts for the majority of the variability in the stable isotope dataset.

The spatial distribution of the $\delta^{18}O$ content of both the unconfined and confined aquifer is shown in figure 21 and 24 respectively. For the unconfined and confined units $\delta^{18}O$ values are most depleted in the topographically higher areas in the south-east of the study region where no irrigation occurs compared to the flat topographically low-lying areas which are located north-west and west in the study region where irrigation practices prevail. This indicates that rainfall, topography and geomorphology condition of the landscape control recharge mechanism. The spatial distribution of $\delta^{18}O$‰ values of the unconfined aquifer illustrates that recharge is occurs from the south-east and flows from the south-east and flows towards the Berg river, Saldanha Bay and the Lagoon. The stable isotope composition agrees with postulated flow direction from previous researchers (Timmerman, 1985; Seyler *et al*, 2016).

It is observed that there are 4 distinct groundwater signatures (Figure 25). Groundwater samples in group A plot between the GMWL for all the unconfined and confined aquifers. This result shows that isotopically there is no significant difference between these aquifers. If aquifers of different depths in the same aquifer system have the similar isotopic composition but vary significantly in depth and is not in hydraulic connection, suggests that groundwater in the confined aquifer experiences extremely slow flushing of groundwater and maintains a secular average isotope composition close to present day rainfall of semi-arid rainfall values (Verhaegen, 1992). The lack of significant difference between isotopic composition of groundwater of shallow and deep groundwater in group A, suggest the aquifer units were recharged during the same climatic event and that precipitation is the dominant source of recharge for both the unconfined and confined aquifers. This finding is similar to that of Keesari (2017) who found that groundwater in unconfined and confined aquifer were in the same range for an coastal alluvium aquifer in the Punjab state of India. The groundwater $\delta^{18}O$ values of the unconfined aquifer are -4.31‰ and of the confined are -4.23‰. These $\delta^{18}O$ of groundwater potentially represent historical averages of rainfall $\delta^{18}O$ values as the rain droplets experienced greater evaporation effects due to increased temperature and decreased relative humidity.

Group B is groundwater of the unconfined and bedrock aquifer that have experienced a significant evaporation effects prior to infiltration. The range for groundwater in the confined aquifer is similar to that of the unconfined aquifer which indicates that groundwater is recharged from a source that is exposed to evaporation effects prior to infiltration such as rainfall. This would be possible if through focused recharge mechanism or if the unconfined aquifer is directly superimposed over the basement aquifer where the clay and LAU are locally absent at the topographic high. This geological conformation was postulated by DWAF (2009) and has been confirmed by recent drilling by the Institute for Water Studies at the University of the Western Cape. The isotopic composition of bedrock aquifer suggests that the bedrock aquifer is recharged by piston flow and flows laterally downgradient where groundwater was sampled. The groundwater δ^{18}‰ is -2.45 before rainfall and in August -2.61. The results of the stable isotope support a similar hypothesis highlighted by Weaver and Talma (2004) that groundwater recharge to the confined aquifers occurs locally and not from regional flow from Franschhoek Mountains some 50km away.

Group C is made up of all rainwater and sampled collected during the study period. Groundwater sampled from a shallow borehole close to the coast (G46106) exhibits similar isotopic composition falls within this group which suggests the main recharge mechanism in this region. This borehole was drilled in close proximity to the Vredenburg pluton. This suggests that in winter months the runoff generated by the impermeable pluton is a source of recharge for the unconfined aquifer. The groundwater is most enriched in the pre-rainy season (δ^{18}O:-2.44‰) and the average δ^{18}O values rainfall for the region was -1.33‰ are similar suggesting that groundwater is recharged directly by local rainfall. The groundwater plots above the LMWL and GMWL which suggests that groundwater has experienced negligible to no evaporation effects prior to infiltration. The groundwater that was sampled could signify a recharge signal from previous year's rainfall at high elevations such as the Vredenburg Pluton which directly infiltrated into cracks and fissures at the surface and flowed via fractures in the subsurface.

The surface water samples collected from the Langebaan Lagoon and the Berg River plot to furthest to right of the GMWL and are the most enriched samples (Group D). This is expected due to the immediate evaporation of surface waters due to direct exposure to the atmosphere. A groundwater sample (BH2) sampled from a borehole that was historically thought to be part of the confined system due to the borehole drilling logs clusters with the rest of the surface water samples of Group D. The groundwater δ^{18}O values are significantly enriched in heavy isotopes (0.52‰) and has similar isotopic composition to surface water from the lagoon (δ^{18}O:1.3‰). The groundwater isotopic composition at BH2 indicates that the groundwater is not representative in isotopic composition as the groundwater in the rest of the WCAS. Since the groundwater and lagoon have similar isotopic composition it can be deduced that a hydraulic connection. The lagoon water is postulated to be the source of recharge to deep groundwater at the lagoon due to the similarity in isotopic composition or due to seawater intrusion. According to Satrio (2017) the $\delta^{18}O$‰ composition of seawater is close to 0‰ which is in the same range as groundwater at the Lagoon. The lagoon is sourced from seawater from the Atlantic Ocean and groundwater discharge from the unconfined aquifer and exposed to the evaporation which is why the lagoon is slightly more enriched than deep groundwater. The significant difference in the isotopic composition of groundwater at the lagoon and the rest of the WCAS confirms that a saline-freshwater interface exists in deep geological zones, which is controlled by deposition of the clay layer and calcrete lenses. The groundwater of the upper aquifer at the Geelbek Lagoon has similar isotopic composition to the rest of the WCAS. The difference in groundwater composition at BH2 compared to the rest of WCAS indicates that groundwater at the lagoon was recharged under a different and more recent climatic event than the rest of the WCAS due to its uncharacteristically highly enriched groundwater (Kpegli, 2017).

The water that was sampled from the Berg River had significantly different isotopic composition than groundwater of the WCAS. The groundwater $\delta^{2}H$‰ and $\delta^{18}O$‰ values for the WCAS (excluding BH2) ranged from -18.8‰ to -3.38‰ and –4.34‰ to -2.44‰ respectively and the Berg River $\delta^{2}H$‰ and $\delta^{18}O$‰ values ranged from 4.7‰ to 23.1‰ and -0.34‰ to 4.98‰ respectively. The results show that surface water is not a source of recharge for the unconfined and confined aquifer in the region. The results of the stable isotopes validate the groundwater flow patterns illustrated in the piezometric map (Figure 11) which illustrates groundwater flow discharges into the Berg River. According to Winter et al (1998) the Berg River experiences gaining conditions as river water does not infiltrate and recharge the aquifer which is confirmed by significant difference isotopic composition between surface and groundwater. It has been pointed that in times when the river is in flood then the hydraulic in the unconfined aquifer will be reversed and surface water is likely to recharge groundwater. Due to the drought conditions and decrease of rainfall that the region experienced during the data collection period it was not expected that the river water would recharge the unconfined aquifer, validating that stable isotopes of groundwater can be used to assess the interconnectivity between the two water bodies.

The direct relationship between δ^{18}‰ and $\delta^{2}H$‰ are described the GMWL to which all samples are compared to. The GMWL serves as a global reference to define evaporative history of water sources sampled in a study. The slope of the equation 2 represents the degree of evaporation of the falling raindrop or surface waters before recharging groundwater and a slope less than 8 suggests evaporation effects (Keesari, 2017). The points representing the groundwater for the unconfined when plotted define a regression line $\delta D=2.65\delta^{18}O-6.23$. The value of the slope is 2.65, which is lower than that of the GMWL which reveals that prior to infiltration groundwater experiences significant evaporation effects. The points representing the groundwater for the confined aquifer when plotted define a regression line $\delta D=4.92\delta^{18}O+2.6$. The slope of the equation represents the degree if evaporation before groundwater infiltrates and forms recharge. The value of 4.92 is higher than the slope of 2.65 which demonstrates that the unconfined aquifer experienced greater evaporation effects than the confined aquifer-which was expected. This illustrates that in the unsaturated zone at the surface there is a great deal of evaporation soon water before infiltration. This evaporation rate is significant as groundwater of the unconfined and confined aquifer plot below the GMWL which groundwater enriched in heavy isotopes. The significant rate of evaporation in the study is linked to the significant evaporation of water infiltrating, increased potential of evaporation in the vadose zone or at the water table due to decreased rainfall and increased temperature because of the drought and semi-arid conditions in the study area.

5.5.3 Groundwater residence time using radiogenic isotopes

Tritium values of the unconfined aquifer ranged from 0.0-1.2T. U, 0.0-0.8 for the deep confined aquifer and 1.2T.U for a single rainwater sample collected the winter months from a rain gauge in Aurora (G10K). The spatial distribution of tritium in the unconfined aquifer and confined aquifer is depicted as figure 28 and figure 29 respectively. From figure 28 groundwater in the unconfined is the younger in some locations than others. The tritium results that at G46060 (1.2T.U) is most recently recharged by precipitation as groundwater tritium content is similar to rainfall (1.4T.U). This implies recent contributions of rainfall or persistent irrigation return flow as the recharge mechanism and thus sort transit time through the unsaturated zone. The tritium activity of groundwater samples in the WCAS suggest that there are five possible recharge mechanisms, recent groundwater recharge by rainfall to the unconfined aquifer or irrigation return flow (G46060), or groundwater recharged by surface water to the unconfined aquifer (G33323), possible recharge to confined aquifers via upward leakage from the basement or due to absence of clay layer (G46029) or recharge from outcrops of Malmesbury which outcrops in the north to the bedrock aquifer or there is no clay layer and confined aquifer in the east at Hopefield and the bedrock aquifer is recharged from leakage from the unconfined aquifer. The tritium content in the

WCAS does not correlate with continental or altitude and geological conformation of the WCAS is the limiting factor for tritium content in groundwater.

The spatial distribution of groundwater of the unconfined aquifer illustrates that there is admixture of submodern with modern groundwater which is not expected due to exposure of aquifer to direct rainfall. The spatial distribution illustrates that complexity of stratigraphy. The tritium results agree with distribution of complex succession of aquifer-aquitard of clay and peat layers of the unconfined aquifer. A similar result was found Yusuf (2018) who investigated the residence times of coastal unconfined sandy aquifer in Nigeria and found that the reason for anomalous occurrence of undetectable tritium in shallow groundwater is due to probable mixture of recently recharged (post 1960) and old groundwater due to the presence of relatively impermeable layers which increases the residence times and enables the disintegration of tritium content of groundwater. The groundwater tritium activity correlates well with the geological confirmation for the unconfined aquifer a show that in topographically middle portion of the aquifer is the most permeability which enhances the short residence times and direct recharge. The variable tritium content in the upper unconfined reflect both immediate and delayed recharge to the unconfined.

Low tritium in the confined aquifer indicates that the groundwater is the same age as the unconfined aquifer which indicates the source of recharge of recharge is similar. A sample from the deep bedrock aquifer (G46105) and the confined aquifer (G46029) results show that tritium content is a mixture of sub modern and recently recharged groundwater. The groundwater results for the bedrock and confined aquifer were 0.8T.U and 0.7T.U respectively which indicates that vertical percolation due to poor well construction or due to the absence of clay layer at these sites (Keesari, 2017; Clarke and Fritz, 1997). The drilled geological logs from the Department of Water Affairs illustrate that a thick clay layer does exist in the region where these boreholes are located. The tritiated groundwater in the bedrock aquifer correlates well with stable isotope composition that there is a hydraulic connection with the deep aquifer and the land surface as water sampled for isotopes exhibited effects of evaporation of groundwater prior to infiltration. These results imply that groundwater in the bedrock aquifer is recharged by source from contains precipitation water from the 1960's (Keesari, 2017).

Results of groundwater with near zero tritium content have been in circulation for a long time and its source of recharge is not present day precipitation (Clarke and Fritz, 1997; Yusuf, 2018).

Generally the confined aquifer has longer residence time as most of the samples range from 0.0-0.3T.U which indicates that groundwater is older than detected age for tritium and that tritium has disintegrated due to its half-life.

Boreholes that penetrated the unconfined and confined aquifer at the same location were selected for this study to understand the distribution of environmental tracer concentration at different depths. The tritium data revealed that at G46029 groundwater in the deep aquifer is considered submodern with a portion of modern recharge (0.8TU) whereas groundwater in the unconfined aquifer is considered as submodern (0.3TU). Therefore, the hypothesis that the unconfined aquifer is source for tritiated groundwater in the confined aquifer is rejected as the deeper aquifer shows that it was recharged by modern precipitation waters that does not originate from the aquifer directly above. This result suggests that the migration of tritiated groundwater to the confined aquifer due to upward leakage from the bedrock aquifer or from downward leakage from an abandoned borehole that penetrates the unconfined aquifer at another location where the clay layer is absent. Talma and Tredoux (2009) had the same reasoning when understanding high variability of ^{14}C content in groundwater of different boreholes sampled at the same depth. The high tritium content in the boreholes that penetrate the confined aquifer are all located adjacent to the Malmesbury Shale-Granite Contact. The lineament could possibly act as a conduit for regional local groundwater flow and recharge the bedrock aquifer through mechanism where exposed at the surface in Vredenburg or Darling. From the stable isotope and tritium trends the results show that a hydraulic interconnection between the unconfined, confined and the confined and land surface is observed. The tritium activity of rainwater is considered to be near pre-bomb levels as atmospheric tritium was recorded as 100T.U in the 1960's. The rainfall tritium content of groundwater in the WCAS is in agreement with reported tritium content of 2-3T.U (Talma and Van Wyk, 2013).

5.5.4 Radiocarbon

The radiocarbon isotope was used in this study to identify medium- and long-term residence times. Radiocarbon allows for the determination of water residence time over timescales of though 30 thousand years(Ayadi, 2017).

The radiocarbon content of the groundwater samples in the unconfined aquifer ranged from 22.9-61.2pMC, 0.0-17.6 for confined aqiufer and 59.1 for groundwater sampled close to the lagoon.

The spatial distribution of radiocarbon for the unconfined aquifer and the confined aquifer is depicted in figure 31 and 32 respectively. Groundwater radiocarbon contents correlates well with depth, better than stable isotope and tritium content its as its long half-life discerns residence time that are more realistic groundwater age. This reported result is similar to other researchers who have used the same environemental isotopes to constrain groundwater flow and characterise groundwater recharge in coastal alluvium hydrogeolgical environment(Kpegli, 2017; Ayadi,2017; Yusuf, 2018).

The ^{14}C content of groundwater in WCAS is highest in the unconfined aquifer and correlates well with tritium content in the same unit except for groundwater at the lagoon where the tritium activity and ^{14}C content are inversely proportional to each other.The ^{14}C content in the unconfined aquifer indicates that that groundwater is of modern age and that residence times is short.Groundwater in the unconfined aquifer is represntative of groundwater that has been recharged during and after nuclear tests occurred. The ^{14}C results also illustrate that the permeability of the sand aquifer in the region, especially in the topographically middle portion of the aquifer has good permeability locally which enhances the short transit time of groundwater in the unit.

The ^{14}C content of groundwater in the deeper confined aquifer of the EAS and LRAS is generally lower than the unconfined aquifer- which was expected due to the sequence of geological deposition. Moreover, the groundwater of the EAS has a longer residence time and is considered older than the LRAS. This result is in agreement with the geological conformation of the basal gravels of the Elandsfontyn formation which suggests that the LRAS is thicker and larger in areal extent so groundwater residence time is shorter as virtue of the geology(Timmerman, 1985; DWAF, 2008;Seyler et al, 2017). From ^{14}C trends the results suggest that there is negligible to hydraulic interconnection between the LRAS and EAS due to the the significant difference in ^{14}C content. This is result is in agreement with borehole data that shows that the basement rises between the two paleochannels to a minimum of 0mamsl (DWAF, 2008) .The distinct ^{14}C content groundwater of the unconfined and confined aquifer indicates that there is lack of mixing due to the significant difference in ^{14}C content of groundwater sampled at the same location that penetrate different units at different depths at the same location.

Like tritium, the natural concentration resulted from thermonuclear testing in the early 1960's and therefore the elevated ^{14}C content in groundwater indicates recent recharge (Kendall and

McDonnell, 1998; Yusuf, 2017).The ^{14}C content decreases in paleowater by radioactive decay hence the usefulness of the isotopes as an age determination tool.For recently recharged water the ^{14}C content is expecetd to be close to or above 100% because ^{14}C is derived from soil CO_2 and it is likely to contian bomb ^{14}C(Mook,2010;Clarke and Fritz, 1997;Talma and Tredoux, 2008).

Previous investigations by Talma and Tredoux (2009) and the present study the allow for a temporal comparison in groundwater ^{14}C content from a borehole drilled into the Malmebury Shale Bedrock Aquifer(G46105). From the results it can be seen that there is a slight decrease in the radiocarbon in the bedrock aquifer from 2.6pMC in 2009 to 0.0pMC in 2017. The decrease in radiocarbon in the bedrock aquifer suggests that older groundwater with longer residence time exists in some part of the aquifer compared to 2008. According to Kpegli et al (2017) a change in the radiocarbon content is generally due to effects of excessive abstraction as younger water is pumped out of the aquifer which had caused older water to be captured in the system as groundwater moves downgradient. It is observed in other coastal aquifers with alternating sand and clay layers in Benin that due to over abstraction of groundwater radiocarbon content increased within a 30 year period, suggesting that some parts of the aquifer younger groundwater exists and that this young water is captured by the system (Kpegli et al, 2017).

The ^{14}C content measured in the groundwater does not show any trends with altitude or the piezoetry in the region. The ^{14}C content in groundwater does exhibit continental trends as the measured radiocarbon content was elevated at groundwater sampled close to the coast from two semi-confined boreholes. According to Atkinson et al(2017), the residence time of groundwater in the confined aquifer generally increases away from the recharge area. Downgradient from the recharge area and groudnwater sampled close to the coast had the highest measured pMC ^{14}C content at 59.1pMC(BH2)at the Geelbek Lagoon and at Saldanha Bay was 61.2(G46106). The radiocarbon is high at coastal sites due to the due to the dissolution of calcrete layers as fossilised marine shells naturally contributeto the carbonate reservoir of groundwater at the coast(Geyh, 2000) . The corresponding tritium activity of at the lagoon and close to Saldanha Bay were 0.0TU and 0.6T.U respectively. Elevated groundwater ^{14}C groundwater that is titriated indicates that that a component of groundwater is fresh and more than 50 to more than a hundred years old (Yechieli et al, 2001; Yechieli et al, 2007). At the Geelbek Lagoon where elevated 14C was measured and groundwater tritium is 0.0TU suggests that infact brackish groundwater was not being sampled, but seawater.The measured ^{14}C in seawater was measured at 100-117pMC from the Medditerraenian Sea in Israel, and is expected to be lower in the southern hemisphere (Yechieli et al, 2001). Generally the tritium activity of seawater is near zero. The stable isotope, tritium and radiocarbon trends indicate that groundwater at the lagoon is isolated and not hydraullically connected to the confined aquifer of the WCAS.

Chapter 6-Recharge estimation using the CMB technique

6.1 Introduction

Chapter 6 of this study presents and discusses the results which were obtained during the quantitative assessment of recharge of the WCAS. This chapter addresses objective 2 the study, which focused on applying the Chloride Mass Balance method using the saturated zone approach (Adams *et al*, 2004). The central argument presented that due to spatial distribution of groundwater chloride a fraction of chloride in precipitation and dry deposition is transported to the water table by downward flow of water. This section will highlight the use of the CMB technique to characterize and estimate recharge both at local and regional scale. CMB was used for the unconfined aquifer as it is the most recently recharged and would provide plausible recharge estimates with regard to shorter flow paths. Limitation of the CMB technique will provide specific spatiotemporal recharge estimate. General information on recharge estimates are lacking during the drought period.

6.2 Key results chloride concentration

6.2.1 Rainwater

The chloride concentration of rainwater is one of the inputs required by the CMB technique. Figure 33 illustrates the concentration of chloride in rainwater for these rain gauges for August and November 2017. The average precipitation measured in the West Coast for from January 2017 to February 2018 was 158.5mm/annum. Chloride concentrations in rainfall ranged from 10-27mg/L. The highest concentration of chloride in rainwater was measured in August from rain gauge G46092-RF at 110mg/L, which is rain gauge closest to the coast in the west and represents a statistical outlier. The mean rainwater chloride concentration was 17.90mg/L in the study area, which represents the average rainwater chloride concentration that reaches the land surface of the catchment. The lowest concentration of chloride in rainwater was measured from rain gauge G46024 at 10mg/L in November 2017. This rain gauge is situated 21km from the coast and is the rain gauge situated topographically high lying area in the east. A good correlation exists between the amount of rainfall measured (seasonality) and chloride concentration (figure 33 and figure 34). From these illustrations it can be seen that the rainfall chloride concentration and rainfall amount are directly, as high chloride concentrations are associated with high rainfall events. This is attributed to the dilution of aerosols during high rainfall events.

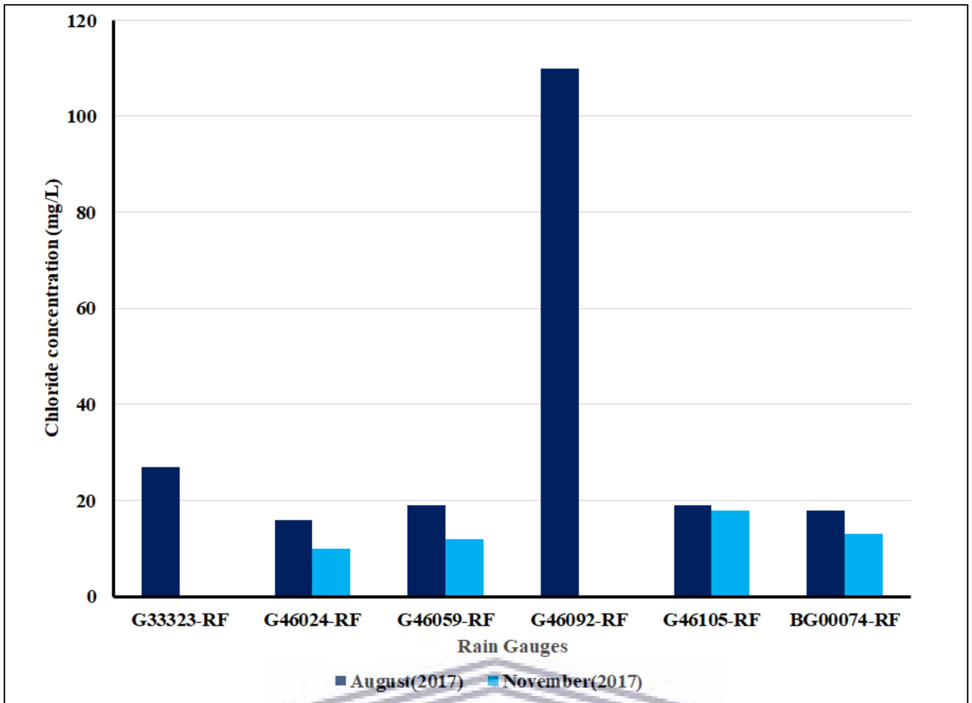


Figure 32: Rainfall chloride concentration at rain gauges in the West Coast

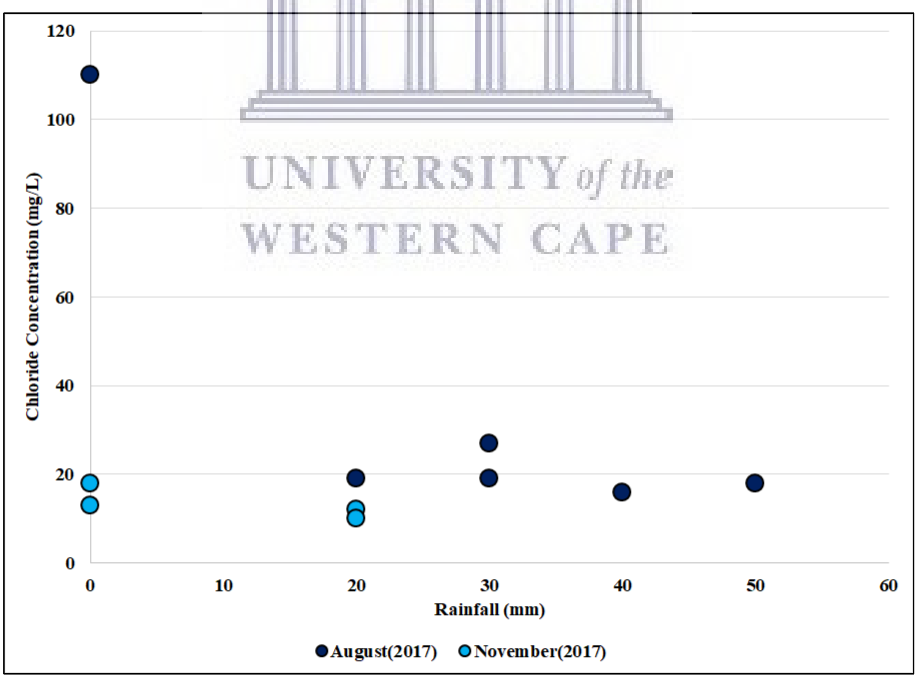


Figure 33: Measured rainfall chloride concentrations versus measured rainfall amount for individual samples

6.2.2 Groundwater

Figure 34 illustrates the chloride concentration in groundwater sampled from monitoring boreholes in the West Coast. The groundwater chloride concentration ranged from 16-489mg/l with a mean chloride concentration of 183.5mg/l. Regionally, the groundwater concentration is highest in boreholes sampled from the LRAU than the EAU (Appendix 5.1a). The results also indicate that the primary aquifer generally has higher chloride concentration than in the confined aquifers (Appendix 5.1a). Groundwater chloride concentrations tend to increase during or after the winter rainfall months of August and September and decline during the low rainfall months of February. The mean groundwater chloride concentration Figure 34 provides a summary of chloride concentration at each sampled borehole. Appendix 5.1 illustrates that the topography has a direct relationship with groundwater chloride concentration as groundwater chloride concentration decreases with increasing elevation. The mean chloride concentration in monitoring borehole G33323 for the period of May 2017 to February 2018 was 407.25 mg/L, the borehole is unconfined, is situated 6mamsl and 16km from the Coast. Comparatively, the unconfined monitoring borehole G46024 has a mean chloride concentration of 72.75mg/L is situated at 93mamsl and is 21km from the coast.

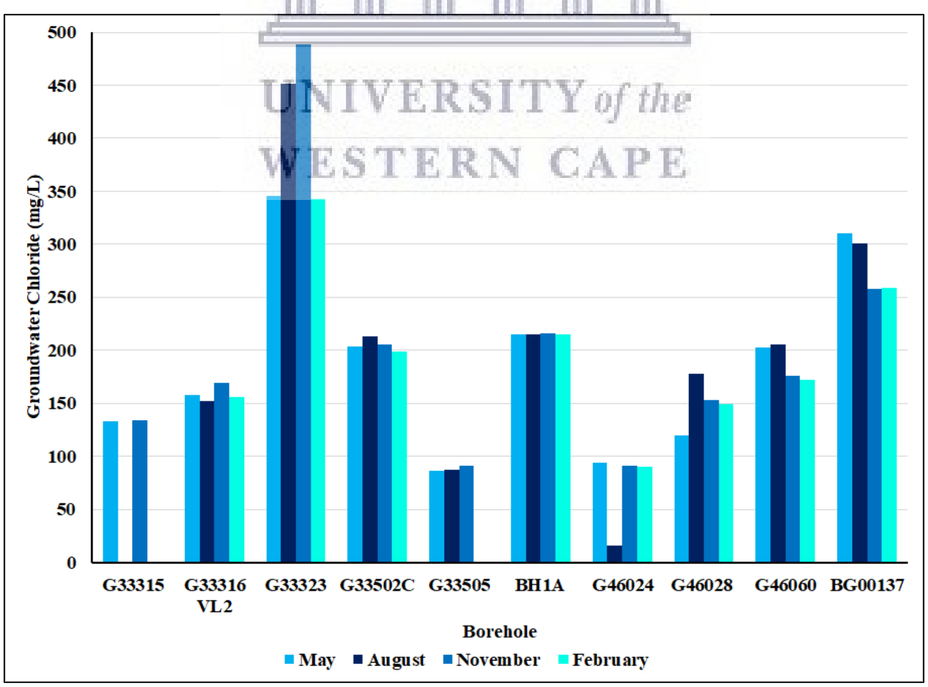


Figure 34: Groundwater chloride concentration variability for the duration of sample period(May 2017-February 2018)

Table 8: Groundwater chloride concentrations (mg/L) for the unconfined aquifer

Borehole	Mean	Min	Max	Std Dev	N
G33315	133	133	134	0.71	2
G33316 VL2	157	152	169	7.27	4
G33323	344.5	343	489	74.11	4
G33502C	201.5	199	213	5.80	4
G33505	86	86	91	2.65	3
BH1A	215	215	216	0.50	4
G46024	92	16	94	37.87	4
G46028	134.5	120	178	23.76	4
G46060	187.5	172	205	17.42	4
BG00137	284.5	258	310	27.39	4
					∑=37

6.2 Groundwater recharge estimates using CMB technique

By obtaining the results in the above sections, recharge can be calculated using CMB methodology is described in section 4.4.5. Table 9 illustrates the recharge estimates for all boreholes sampled from 2017-2018 for chloride analysis in the alluvial unconfined where the influence addition of seawater -chloride had no effect. The recharge estimates of ten boreholes sampled for chloride analysis was obtained using the area weighted mean chloride of rainwater for a specific rain gauge, the total annual rainfall measured from January 2017 through February 2018 from 6 rain gauges and the mean groundwater chloride concentration for each borehole from May 2017 through February 2018. The results of the recharge estimates ranged from 1.53 mm to 11.55mm which represents 1.17% to 5.35% of the total rainfall for the study area using the CMB technique. The mean regional groundwater recharge was estimated at 5.15mm/annum and 3.25% of the average rainfall (158.5) for the West Coast.

Table 9: Groundwater recharge quantified using the CMB Method

Groundwater Samples	Average CL_{gw} (mg/L)	CL_p Aug	Nov	P(at nearest rain gauge)mm	Average Weighted P_{cl}	Recharge (mm/annum)	Recharge (%)
G33315	133.5			191		6.74	3.53
G33316 VL2	158.75			191		5.67	2.97
G33323	407.25			170		1.99	1.17
G33502C	205.25			191		4.38	2.30
G33505	88			191		10.23	5.35
BH1A	215.25			70		1.53	2.19
G46024	72.75			230		11.55	5.02
G46028	150			150		4.07	2.71
G46060	189			150		3.28	2.19
BG00137	282			140		2.02	1.44
Rain Gauge							
G33323-RF		27			4.76		
G46024-RF		16	10		3.65		
G46059-RF		19	12		4.13		
G46092-RF		110			0.00		
G46105-RF		19	18		4.07		
BG00074-RF		18	13		4.71		

6.3Discussion

These rainwater chloride results illustrate that rainwater with elevated chloride concentration was measured at topographically low areas compared to rainwater with low chloride concentrations measured at topographically high areas. Recharge was estimated highest at topographically high area and in these areas' groundwater chloride fluctuated significantly between seasons suggesting that during winter months the alluvial unconfined aquifer receives active recharge. This relationship correlates well with research from previous investigations that applied the CMB method in a coastal aquifer (Weaver *et al*, 2005; Adams *et al*, 2004).The distance from the coast is a major control on rainwater chloride concentration. Rain gauge G46092-RF is 10km from the coast and rainwater chloride concentration was measured at 110mg/L in August 2017 whilst rain gauge G46024-RF which is 21km from the coast with the lowest measured chloride concentration at 10mg/l. Rain gauge. Rain gauge G46092-RF was considered outlier and was excluded from recharge estimation method as indicators of contamination were observed. Groundwater from two shallow boreholes (G46092 and G46106) were excluded from the recharge investigation as the groundwater at the coast ranged from 1250-3320mg/l. This result illustrates that the groundwater closest to the coast is characterized by highly saline groundwater and is the result of marine regression and transgression and seawater intrusion (Adams *et al*, 2004).Weaver & Talma (2005) measured rainwater chloride concentration from rainfall collectors situated at the Langebaan Wellfield and Hopefield which are slightly higher when compared to rainfall chloride results for a rain gauge located at the Langebaan wellfield for the present study. The rainwater chloride concentration shows the continental effect and seasonal effects.

Groundwater chloride in the West Coast is controlled by position in the landscape, distance from the ocean, land use and seasonality. Groundwater chloride concentrations can provide into recharge mechanism for the study area. Table 9 illustrates that monitoring borehole in G46024 was most recently recharge due to the low groundwater chloride concentration in 2017. Borehole G33323 which has the highest measured chloride concentration, which is an indication that recharge, is delayed or that recent recharge has not occurred. This suggests that highest rates of recharge occur in high elevation areas where the concentration of groundwater is low and recharge occurs in the wet season. The maximum chloride concentration of groundwater was measured in months during the highest rainfall period month (August) or during the onset of the dry season (November). Groundwater sampled during the dry season (February) and during the onset of the wet season (May) generally had the lowest chloride concentrations in the study area. The elevated groundwater chloride concentration in response to increased rainfall provides insight into the recharge mechanism for different aquifer units. The increase in chloride concentration in groundwater of the unconfined aquifer is indicative of recharge by diffuse piston-type recharge. The response of increased chloride concentration in groundwater in confined aquifers in high rainfall month's rainfall suggests that recharge occurs focused localized recharge occurs through preferred pathways. This statement is evidenced by the fluctuation in water levels of boreholes in the confined LRAU (G46059 and G46059).The same relationship was observed in groundwater chloride concentration in basement aquifer (G46105). The hard rock Malmesbury shale forms the geological basement. Based on the elevated response of groundwater chloride to increased rainfall, it seems that focused indirect recharge mechanism from fractures at the surface form preferred pathways for rainwater to replenish the basement aquifer or recharge occurs where the alluvial unconfined aquifer overlies the basement where the clay of the Elandsfontyn Formation and lower confined aquifer are absent. This result is supported by the stable isotope composition of groundwater in the bedrock aquifer.

The overall mean groundwater recharge was estimated to 5.15mm, which represents 3.65% of the total mean annual rainfall for the West Coast. The recharge estimates obtained in this study are significantly lower than previous groundwater recharge investigations done by Weaver & Talma (2005). Weaver and Talma used the CMB Method in the coastal aquifer of the LRAS and recharge was estimate at 9.7% to 13.5% of the annual rainfall. In 2008 DWS estimated recharge at 5% to 8% for LRAU using water balance methods and GIS techniques such as GRAII. Comparatively, recharge estimates of the CMB method and Water Balance Method indicate that the CMB slightly overestimates recharge in coastal environments. Du Toit and Weaver (1995) estimated recharge at 8% using water level data and at 12% using reverse modeling techniques at Saldanha. Timmerman (1985) and Vandoolaeghe and Bertram (1982) estimated recharge for alluvial aquifers in Atlantis, south of the study area under investigation and used these recharge estimates to represent recharge to the LRAU and EAU as the aquifers are geologically similar, Although the Atlantis aquifer received most of recharge from massive unvegetated coastal dunes. Timmerman estimated recharge at 5% to 10% using unsaturated model and Vandoolaeghe estimated recharge at 26% using water balance methods. Conrad et al (2004) estimated recharge at 5% to the coastal aquifers of the northern Sandveld using the CMB method.

Chapter 7 Conclusions and Recommendations

7.1 Introduction

A conceptual model consists of a set of assumptions that verbally and or visually describe the hydrogeological environments, based on field observations and data interpretation (Petersen, 2012; Adams et al, 2004). In this study a conceptual model of groundwater recharge processes for the West Coast Aquifer System (WCAS). The development of the conceptual model attempts to describe what the recharge mechanism is and how much groundwater recharged occurred from May 2017 to February 2018. In this study a hydrochemical and isotope approach was used to derive a hydrogeological groundwater conceptual model for the WCAS.

7.2 Synthesis of Conceptual Model

A conceptual model consists of a set of assumptions that verbally or visually describe the aquifer systems based of field observation and data interpretations (Adams *et al*, 2004). In this study a conceptual model of groundwater recharge processes for the WCAS was developed. The conceptual model attempts to answer the spatial and temporal occurrence and the dominant recharge mechanism (figure 35). According to Healy (2010) the factors that influence a conceptual model should include climate, geology, topography, hydrology, vegetation and land use. All these factors were all included in the present study.

The composition of environmental isotope reveals that the WCAS is complex and comprises of different recharge sources. The piezometric map (figure 10) illustrates that groundwater flow from the water level high on the east towards the Atlantic Ocean in the west. The WCAS is made up of sequence of heterogeneous geology alternating sand and clay layers :1)a regional unconfined aquifer that is interbedded with peat and calcrete lenses; 2) a clay aquitard; 3) a southern (EAS) and a northern paleochannel which is incised into the bedrock aquifer composed of Malmesbury Shale and Cape Granite Suite. From the environmental isotope trends a simplified conceptual model of the dominant groundwater recharge process a surface groundwater interaction are described for the WCAS.

Groundwater in the WCAS occurs primarily during the winter rainfall months (June-August) with no recharge occurring during the dry summer months (December-April). Recharge occurs during cumulative rainfall of 80-140mm. The stable isotope illustrates that although there was significant decline in rainfall due to drought conditions the amount of rainfall was sufficient to generate recharge. Combination of environmental isotope concentration used in this study suggest that dominant recharge mechanism that occur in the unconfined aquifer is direct recharge via piston flow. Direct infiltration occurs where peat and calcrete lenses are absent and where these layers are present delayed regional flow is the source of recharge. Variable residence times suggest that peat and calcrete deposition at the surface act as impermeable layers that restrict recharge to the unconfined aquifer. Moreover, this is the reason submodern groundwater is found upgradient and modern water which is found at topographically lower portions of the aquifer. Depleted isotope signatures indicate that for the unconfined aquifer recharge originates from the topographic high portion of the aquifer in the south and flows towards the Geelbek Lagoon, Saldanha Bay and the Berg River as groundwater reveals a more enriched signature. A comparison of rainwater tritium activity and groundwater and historical stable isotope composition confirms that groundwater for the WCAS is derived from local low elevation precipitation.

Groundwater of the unconfined aquifer in the north is not recharged by the perennial Berg River as the hydraulic gradient is lowered when there is decreased flow when drought occurs. The stable isotope results indicate that the Berg River is consistently fed by groundwater which contributes to baseflow throughout the year. The component of modern water from groundwater sampled in from the floodplain of the Berg River provides evidence that historical recharge has occurred when the Berg River is in flood and the hydraulic head in the river is higher than the groundwater of the unconfined aquifer. In the south west the isotope composition of groundwater is recharged indirectly via preferential pathways by the lagoon. The results indicate that the groundwater at the lagoon is detached from the WCAS and was recharged under different climatic condition as the rest of the WCAS. Groundwater residence times at the lagoon reveal that water is more 50-100 years old.

Groundwater in the confined aquifer is recharged indirectly by downward leakage where clay layer thin or absent and groundwater movement is extremely slow as $\delta^{18}O$‰ values are similar to groundwater of the unconfined aquifer and present-day rainfall. It is also possible that groundwater to the confined aquifer is recharged by downward leakage from abandoned boreholes with poor construction where the clay is thinnest or absent or from upward leakage from the bedrock aquifer. Groundwater to the bedrock aquifer is recharged indirectly via preferential flow paths in Vredenburg where the bedrock is exposed at the surface. Environmental isotope trends indicate that groundwater recharge occurs indirectly from downward leakage to the bedrock aquifer occurs where the clay aquitard and lower confined aquifer are absent as a component of groundwater is considered to be of modern-day precipitation. It is also possible that water from the surface infiltrates basement geology at the surface, flows through fractures in the subsurface and flows towards the Malmesbury-Granite Contact which acts a conduit that hydraulically connection from the surface and basement. The EAS is considered to be of older groundwater with longer residence time than the LRAS which indicates that groundwater transit time in the LRAS is shorter-possibly due to historical abstraction causing younger water to be captured in the aquifer. The observed environmental tracer trends for the confined and bedrock aquifer prove that vertical interconnection exists between the unconfined, confined and bedrock aquifers. However, there is no lateral interconnection between the LRAS and the EAS which is confirmed by drilling data.

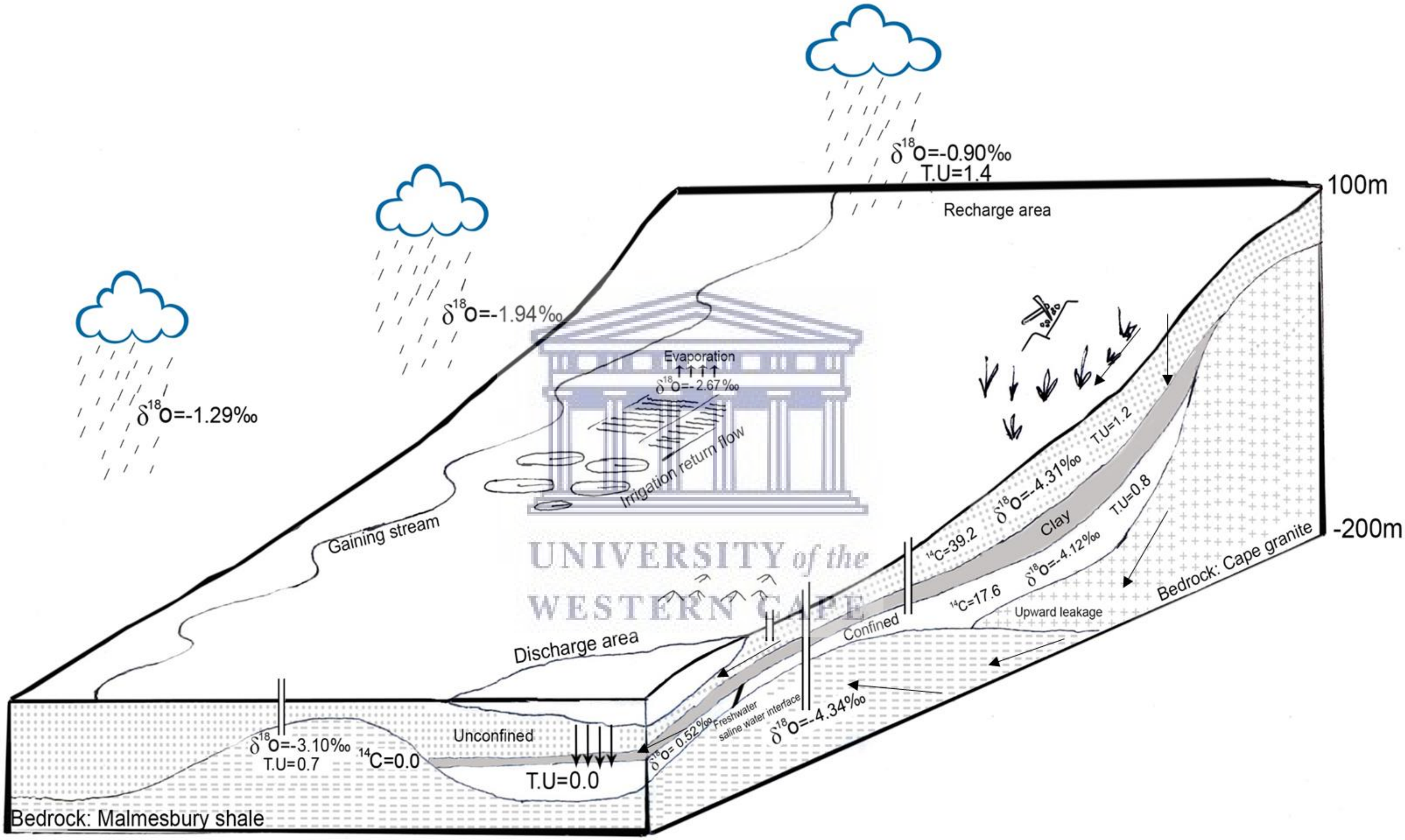


Figure 35: A hydrogeological conceptual of the dominant recharge processes and surface water groundwater interactions associated with different aquifer units of the WCAS.

The estimates generated and application of CMB technique proved to simple and effective method when compared to physical and modelling based methods. Although the method is generally used in non-saline terrestrial hydrogeological environments, the CMB technique provided site specific recharge estimates, which proved useful in the characterization of groundwater recharge zones for the unconfined aquifer. The CMB estimates provided meaningful estimates for the catchment. The method was useful as the estimates that were generated were realistic in terms of the drought and decreased rainfall within the study area during the data collection period.

The results of this study reveal that the monitoring of multi-environmental tracer techniques in the unconfined and confined aquifers could be a powerful tool for identifying how and when recharge processes occur, even coastal hydrogeological environments. The robustness methodology undertaken by the study using the CMB technique provided reliable estimates which can be used for groundwater recharge assessments in other coastal semi-arid catchments.

7.3 Conclusion and Recommendations

It is recommended that pump test techniques are done to assess aquifer hydraulic characterisation and the of abstraction aquifers has a response to water levels in other units which will confirm hydraulic interconnection and identify recharge zones. It is also recommended that geophysical techniques are employed especially in the recharge area at Hopefield to confirm the existence or absence of clay and confined aquifer. Geophysical techniques should also be conducted at the discharge area at the Geelbek Lagoon to assess the extent of detachment of groundwater at lagoon from the EAS. Comprehensive geochemical sampling campaign should be conducted to confirm the extent of potential carbonate dissolution of regional groundwater which could be used to calculate groundwater age which would complement the qualitative residence time assessment done in this study. It is also recommended that a comprehensive radiogenic isotope campaign should be done regionally and should include more boreholes that penetrate all aquifers units, the lagoon, Saldanha Bay and the Atlantic Ocean to confirm the extent of interconnection between groundwater and the lagoon and seawater. Increasing the amount of rainfall collectors is recommended so that there is an increased volume of rainwater that can be captured for environmental isotope analysis and to develop a robust local meteoric water line for the West Coast.

An understanding of groundwater recharge and flow dynamics can help inform sound management decisions. The identification of two separate groundwater systems can be used by groundwater managers to make sound decisions about abstraction and mitigate the looming threat of salinization of groundwater if abstraction was to occur close to the lagoon. The identification of a groundwater capture zone for the unconfined G46060 should influence future land use activities, highlighting the importance for the establishment as the area as groundwater recharge protection zone. Predicted rise in sea levels in semi-arid coastal regions due to climate change exacerbates interventions required to control groundwater abstraction for the WCAS where freshwater is under threat by potential salinization effects. The application of a combination of stable and radiogenic isotope of rainfall, surface and groundwater in coastal hydrogeological environments proves to be valuable to confirm plausible recharge process. The developed conceptual model serves as a guide which contributes to knowledge of dominant spatial and temporal occurrence of recharge, surface and groundwater interaction as well as aquifer-aquifer interconnection in the WCAS

The application of hydrochemical techniques to qualitatively conceptualise has been achieved through the use of environmental isotopes. This study applied environmental isotopes successfully in coastal hydrogeological investigation to establish sources of groundwater recharges, understand the extent groundwater-surface water interconnectivity and constrain plausible recharge mechanism to shallow and deep groundwater units in the West Coast. The application of Chloride Mass Balance (CMB) in the coastal aquifer proved to be useful to quantify recharge estimates in the West Coast Aquifer System as first approximation of recharge. However, this method must be applied in conjunction with other methods such as Water Table Fluctuation Method to validate the recharge estimate. Groundwater in that exhibit the effects of salinization in coastal aquifer should be considered as input for recharge estimation as the method will provide an overestimate of recharge. The CMB should be applied due to its simplicity and relatively low cost in quantifying groundwater recharge and delineating recharge areas in coastal alluvial aquifers, if the investigation considers a comprehensive understanding of hydrogeology and sources of additional chloride in the region.

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Appendix 5.1 Groundwater sampling information and water level measurements

Sampling Information							Water Level(mbgl)			
Water ID	**Aquifer**	**Water Source**	**Latitude**	**Longitude**	**Elevation(mamsl)**	**Borehole Depth(m)**	**May-17**	**Aug-17**	**Sep-17**	**Feb-18**
G46105	Bedrock	Groundwater	-32.9858	18.1891	42	216	13.33	11.04	4.92	13.82
G33502A	Bedrock	Groundwater	-33.1197	18.2476	101	159	27.66	27.94	27.9	27.92
G46030	Bedrock	Groundwater	-33.0353	18.1836	67	119	x	13.48	13.67	13.69
G46029	Confined-LRAU	Groundwater	-33.0089	18.1778	48	98	14.43	x	x	x
G46059	Confined-LRAU	Groundwater	-32.9489	18.2038	35	50	4.27	4.16	3.44	4.45
G46023	Confined-LRAU	Groundwater	-33.0211	18.2659	93	77	3.26	3.02	3.17	3.29
BG00136	Confined-LRAU	Groundwater	-32.9859	18.1894	43	78	15.31	12.76	11.13	15.7
G33317	Confined-EAU	Groundwater	-33.1130	18.2174	78	139	15.55	15.86	15.43	15.31
G33505B	Confined-EAU	Groundwater	-33.0919	18.1914	81	161	26.99	26.51	26.44	26.26
BG00074	Confined-EAU	Groundwater	-33.1243	18.2361	93	102	22.6	22.81	22.86	22.81
BH2	Confined-EAU	Groundwater	-33.1933	18.1269	4	44	1.39	0.48	1.64	1.49
G33323	Unconfined	Groundwater	-32.8855	18.2477	6	63	3.26	3.02	3.17	3.29
G46060	Unconfined	Groundwater	-32.9489	18.2038	35	17	3.81	3.94	4.13	4.2
G46024	Unconfined	Groundwater	-33.0211	18.2659	93	7	7.2	7.34	7.34	7.3
BG00137	Unconfined	Groundwater	-32.9859	18.1894	43	14	1.59	1.76	1.74	1.74
G46028	Unconfined	Groundwater	-33.0089	18.1778	48	33	3.06	x	x	x
G33316VL2	Unconfined	Groundwater	-33.1378	18.1979	72	9	15.55	15.77	15.62	15.33
G33502C	Unconfined	Groundwater	-33.1198	18.2475	101	66	13.27	13.67	13.8	13.61
G46106	Unconfined	Groundwater	-33.0129	18.0568	14	17	5.29	5.46	5.64	5.63
G33315	Unconfined	Groundwater	-33.1380	18.2269	86	145	15.09	17.15	17.11	17.02
BH1A	Unconfined	Groundwater	-33.1860	18.1320	6	13	0.98	0.83	1.16	1.99
G33505	Unconfined	Groundwater	-33.0906	18.1921	81	127	26.43	26.45	28.24	27.28
G46092	Unconfined	Groundwater	-32.9447	18.0876	25	28	1.36	x	x	x
Berg River	*	Surface Water	-32.9070	18.3346	7	*	*	*	*	*
Geelbek Lagoon	*	Surface Water	-33.1912	18.1272	2	*	*	*	*	*
BG00074-RF	*	Rainwater	-33.1242	18.2359	93	*	*	*	*	*
G33323-RF	*	Rainwater	-32.8856	18.2477	6	*	*	*	*	*
G46059-RF	*	Rainwater	-32.9487	18.2039	35	*	*	*	*	*
G46024-RF	*	Rainwater	-33.0211	18.2659	93	*	*	*	*	*
G46105-RF	*	Rainwater	-32.9858	18.1891	42	*	*	*	*	*
G46092-RF	*	Rainwater	-32.9447	18.0876	25	*	*	*	*	*
G10K	*	Rainwater	-32.7186	18.5751	971	*	*	*	*	*

Legend	
x	**not collected**
*****	**not applicable**

Appendix 5.1a Environmental isotope and chemical composition of water samples collected in the West Coast (May-Aug 2017)

			May-17					Aug-17						
Water ID	**Aquifer**	**Water Source**	**δ^2H‰**	**$\delta^{18}O$‰**	**d-excess**	**Cl(mg/L)**	**Alkalinity as $CaCO_3$**	**δ^2H‰**	**$\delta^{18}O$‰**	**d-excess**	**^3H (T.U)**	**^{14}C(pMC)**	**Cl(mg/L)**	**Alkalinityas $CaCO_3$**
G46105	Bedrock	Groundwater	-14.7	-2.45	4.9	119	73	x	x	x	0.7	0	126	140
G33502A	Bedrock	Groundwater	x	x	x	152	192	-14.9	-3.68	14.54		*	155	183
G46030	Bedrock	Groundwater	-15.6	-4.08	17.04	106	144	-16.5	-3.9	14.7	0.2	*	107	142
G46029	Confined-LRAU	Groundwater	-14.7	-3.89	16.42	120	159	-15.2	-3.88	15.84	0.8	*	118	154
G46059	Confined-LRAU	Groundwater	-18.8	-3.97	12.96	136	115	-16.1	-3.85	14.7	0.2	17.6	139	112
G46023	Confined-LRAU	Groundwater	-15.8	-3.53	12.44	110	90	x	x	x	0	x	112	87
BG00136	Confined-LRAU	Groundwater	-16.8	-3.57	11.76	152	17	-13.9	-3.32	12.66	0	x	153	23
G33317	Confined-EAU	Groundwater	-16.9	-4.12	16.06	176	138	-15.2	-3.98	16.64	0.3	3.2	165	160
G33505B	Confined-EAU	Groundwater	x	x	x	96	131	-16.4	-3.75	13.6	0.1	4.9	96	127
BG00074	Confined-EAU	Groundwater	-18.7	-3.77	11.46	145	134	-16.7	-3.96	14.98	0	x	165	104
BH2	Confined-EAU	Groundwater	6.8	0.45	3.2	35700	289	5.5	0.33	2.86	0	59.1	35100	277
G33323	Unconfined	Groundwater	-16.5	-3.77	13.66	346	128	-13.3	-3.36	13.58	0.7	x	451	125
G46060	Unconfined	Groundwater	-14.4	-3.28	11.84	203	164	-16.9	-3.5	11.1	1.2	39.2	205	149
G46024	Unconfined	Groundwater	-18.3	-3.7	11.3	94	53	-15.4	-3.69	14.12	0.3	x	16	
BG00137	Unconfined	Groundwater	-15.3	-3.32	11.26	310	186	-16	-3.53	12.24	0.8	*	301	182
G46028	Unconfined	Groundwater	-14.5	-2.7	7.1	147	157	-11.6	-3.71	18.08	0.3	*	178	161
G33316VL2	Unconfined	Groundwater	-15.6	-3.72	14.16	158	154	-15.4	-4.01	16.68	0	*	152	162
G33502C	Unconfined	Groundwater	-16.7	-3.99	15.22	204	170	x	x	x		*	213	160
G46106	Unconfined	Groundwater	-14.6	-3.39	12.52	3155	337	-14.6	-3.24	11.32	0.6	61.2	3230	338
G33315	Unconfined	Groundwater	-17.6	-3.31	8.88	133	156	-16.8	-4.18	16.64	0.6	*		
BH1A	Unconfined	Groundwater	-14.4	-3.84	16.32	215	192	-16.4	-3.51	11.68	0	22.9	215	187
G33505	Unconfined	Groundwater	x	x	x	86	91	-16.4	-3.92	14.96	0.7	39.9	87	85
G46092	Unconfined	Groundwater	-3.38	-2.44		1250	143	x	x	x	0.1	*	1310	140
Berg River	*	Surface Water	23.1	3.95	-8.5	*	*	*	*	*	*	*	*	*
Geelbek Lagoon	*	Surface Water				*	*	9.2	0.45	5.6	*	*	*	*
BG00074-RF	*	Rainwater				x	x	-6.3	-2.6	14.5	x	*	18	3.1
G33323-RF	*	Rainwater				x	x			0	x	*	27	<2.5
G46059-RF	*	Rainwater				x		-5.3	-2.85	17.5	x	*	19	3.8
G46024-RF	*	Rainwater				x	x			0	x	*	16	16
G46105-RF	*	Rainwater				x	x	-6.1	-2.61	14.78	x	*	19	9.4
G46092-RF	*	Rainwater				x	x	-2.7	-0.87	4.26	x	*	110	352
G10K	*	Rainwater				*	*	*	*	*	1.4	*	*	*

Legend	
x	not collected
*	not applicable

Appendix 5.1b Environmental isotope and chemical composition of water samples collected in the West Coast (Nov-Feb 2018)

			Nov-17					Feb-18				
Water ID	**Aquifer**	**Water Source**	**δ^2H‰**	**$\delta^{18}O$‰**	**d-excess**	**Cl(mg/L)**	**Alkalinity as $CaCO_3$**	**δ^2H‰**	**$\delta^{18}O$‰**	**d-excess**	**Cl(mg/L)**	**Alkalinity as $CaCO_3$**
G46105	Bedrock	Groundwater	-15.1	-3.75	14.9	129	137	x	x	x	119	78
G33502A	Bedrock	Groundwater	x	x	x	155	188	-17.2	-4.34	17.52	155	185
G46030	Bedrock	Groundwater	-16.6	-3.9	14.6	105	145	-16.6	-3.78	13.64	107	138
G46029	Confined-LRAU	Groundwater	-15.8	-3.83	14.84	118	162	-18.3	-4.06	14.18	118	158
G46059	Confined-LRAU	Groundwater	-15.3	-3.48	12.54	136	116	-16.4	-3.24	9.52	137	112
G46023	Confined-LRAU	Groundwater	-15.6	-3.82	14.96	112	89	-16	-3.76	14.08	100	82
BG00136	Confined-LRAU	Groundwater	-15.2	-3.58	13.44	143	32	-17.4	-3.61	11.48	141	29
G33317	Confined-EAU	Groundwater	-16	-3.57	12.56	177	168	-16.1	-3.45	11.5	164	166
G33505B	Confined-EAU	Groundwater	x	x	x	97	129	-17.8	-3.72	11.96	94	128
BG00074	Confined-EAU	Groundwater	-12.1	-3.7	17.5	151	158	-16.2	-3.65	13	145	156
BH2	Confined-EAU	Groundwater	3.9	0.65	-1.3	36750	287	4.6	0.64	-0.52	36400	283
G33323	Unconfined	Groundwater	-16.1	-2.76	5.98	489	135	-16.8	-3.41	10.48	343	122
G46060	Unconfined	Groundwater	-15.1	-3.06	9.38	176	138	-17	-2.54	3.32	172	x
G46024	Unconfined	Groundwater	x	x	x	91	54	-16.3	-3.19	9.22	90	53
BG00137	Unconfined	Groundwater	-15.9	-3.46	11.78	258	188	-15.1	-3.2	10.5	259	188
G46028	Unconfined	Groundwater	-16.1	-3.73	13.74	153	162	-17.5	-3.81	12.98	149	156
G33316VL2	Unconfined	Groundwater	-16.1	-3.25	9.9	169	163	-17	-3.72	12.76	156	155
G33502C	Unconfined	Groundwater	-16.3	-3.82	14.26	205	161	-17.6	-4.31	16.88	199	152
G46106	Unconfined	Groundwater	-14.5	-3.2	11.1	3300	346	-15	-3.38	12.04	3320	335
G33315	Unconfined	Groundwater	x	x	x	134	153	x	x	x	x	x
BH1A	Unconfined	Groundwater	-18.3	-3.57	10.26	216	196	-15.9	-3.94	15.62	215	191
G33505	Unconfined	Groundwater	x	x	x	91	82	x	x	x	x	x
G46092	Unconfined	Groundwater	-16.3	-3.29	10.02	1390	145	-12.9	-3.12	12.06	1290	141
Berg River	*	Surface Water	4.7	-0.34	7.42	*	*	20.9	4.98	-18.94	*	*
Geelbek Lagoon	*	Surface Water	x	x	x	*	*	11.9	2.05	-4.5	*	*
BG00074-RF	*	Rainwater	-0.8	-1.18	8.64	13	3.1	-0.4	-0.23	1.44	*	*
G33323-RF	*	Rainwater	1.2	-0.31	3.68	x	x	x	x	x	*	*
G46059-RF	*	Rainwater	-1.5	-1.03	6.74	12	3.3	x	x	x	*	*
G46024-RF	*	Rainwater	-1.3	-0.9	5.9	10	21	x	x	x	*	*
G46105-RF	*	Rainwater	-3.8	-2.3	14.6	18	4.2	4.4	0.55	0	*	*
G46092-RF	*	Rainwater	-2.3	-1.7	11.3	x	x	x	x	x	*	*
G10K	*	Rainwater	*	*	*	*	*	*	*	*	*	*

Legend	
x	not collected
*	not applicable

Appendix 6.1 Rainfall measurements from selected rain gauges in the West Coast

	Rain Gauge Measurements(mm)					
Monthly	**BG00074-RF**	**G33323-RF**	**G46059-RF**	**G46105-RF**	**G46092-RF**	**G46024-RF**
January	0	10	10	10	0	10
February	0	0	0	0	0	0
March	0	0	10	0	0	10
April	0	10	0	10	0	10
May	0	0	10	0	10	10
June	60	50	40	60	30	60
July	30	30	20	20	0	30
August	50	30	20	30	0	40
September	10	10	10	0	0	10
October	11	10	10	0	10	30
November	0	20	20	0	20	20
December	0	0	0	0	0	0
January	2	0	0	10	0	0
February	28	0	0	0	0	0
∑(mm/annum)	**191**	**170**	**150**	**140**	**70**	**230**