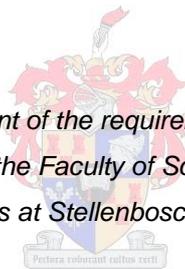


**Salinisation source(s) and mechanism(s) in shallow alluvial aquifers along the Buffels River,  
Northern Cape Province, South Africa**

by

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*Thesis presented in fulfilment of the requirements for the degree of Master  
of Science (Geology) in the Faculty of Science, Department of Earth  
Sciences at Stellenbosch University*



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March 2015

**Declaration**

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## Abstract

Several areas in Namaqualand are affected by elevated levels of salinity; including the shallow alluvial aquifers along the Buffels River catchment. The chemistry of rainwater that recharges these aquifers has low salt-loads, but the groundwater system is very saline. The shallow alluvial aquifers are an important source of water for several communal areas along the river both for domestic and agricultural purposes. Groundwater is also used for the copper and diamond mining activities along the river. Prior to this study, the sources of salinity to the alluvial aquifers and whether salinity can be remediated has not been determined. Possible salinity sources included seawater intrusion, evaporitic salts dissolution, concentrations by evaporation, deep aquifer brines, dissolution of minerals from the aquifer geology as well as salts from anthropogenic activities (i.e. mining).

The source(s) of salinity to the groundwater has been determined using the geochemical as well as the isotopic tracers. The ratios of major ions (i.e. Na/Cl) as well the oxygen ( $^{18}\text{O}$ ), hydrogen ( $^2\text{H}$ ),  $^{36}\text{Cl}/\text{Cl}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes were used in determining the possible solute sources. In addition to these, the chloride mass balance (CMB) method was used to determine the recharge rates to the alluvial aquifers. Furthermore, the groundwater age of the alluvial aquifers was determined using the tritium ( $^3\text{H}$ ) isotope. The groundwater samples have high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which are in the same ranges as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the surrounding granitic rocks indicating water-rock interactions. The  $^{36}\text{Cl}/\text{Cl}$  ratios are low and indicate the dissolution of old salts. The  $^{18}\text{O}$  and  $^2\text{H}$  stable isotopes of groundwater show an evaporative trend with respect to the LMWL, which indicate that groundwater has been evaporated before or during infiltration. Salinity to the shallow alluvial aquifers was found to be mainly derived from the dissolution of rock mass and concentration by evaporation process. The groundwater is relatively young, but there is mixing between old water recharged prior to bomb testing and recently recharged groundwater in some boreholes.

The Chloride mass balance (CMB) method assumes atmospheric chloride is the only source of chloride to the aquifers. However, there is additional chloride to these alluvial aquifers from rock mass dissolution. The estimated recharge rates by CMB method (0.1-3.4mm/a) are therefore underestimated. A simulation model was used to determine the recharge rates based on the annual precipitation that will yield the current measured chloride concentrations in the groundwater. Recharge was found to range from 1-5% of the annual precipitation, which is also low. The CMB method therefore gives significant recharge rate estimates, but they are not accurate and need to be supported by another method.

## **Dedication**

I dedicate this thesis to my beloved parents, Mr Johannes and Mrs Lusia Nakwafila, for always supporting me in my decisions and for the encouragements whenever I felt like giving up. Difficult I was at times; but you never gave up on me. Thanks for teaching me the importance of education and hard work.

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### Abbreviations and symbols

°C – Degrees Celsius

‰ – Per Mil

<sup>16</sup>O – Oxygen-16 (Isotope of oxygen)

<sup>18</sup>O – Oxygen-18 (Isotope of oxygen)

<sup>1</sup>H – Hydrogen-1 (Isotope of hydrogen)

<sup>2</sup>H/ D – Hydrogen-2/ Deuterium (Isotope of hydrogen)

<sup>3</sup>H – Hydrogen-3/Tritium (Isotope of hydrogen)

a.m.s.l - Above Mean Sea Level

CAF – Central Analytical Facility

EC – Electrical Conductivity

GMWL – Global Meteoric Water Line

HNO<sub>3</sub> – Nitric acid

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

LMWL – Local Meteoric Water Line

Ma - Million years

mg/L – Milligrams per litre

mm - millimetre

mm/a - millimetre per annum

mS/cm – Millisiemens per centimetre

PE – Polyethylene

PP – Polypropylene

SAWB – South Africa Weather Bureau

SMOW – Standard Mean Oceanic Water

TDS – Total Dissolved Solids

TU – Tritium Unit

WHO – World Health Organisation

δ<sup>18</sup>O – Oxygen Isotope value (‰)

δ<sup>2</sup>H – Hydrogen Isotope value (‰)

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## Chapter 1: General Introduction

### 1.1 Introduction

Water resources all over the world are deteriorating due to the high salt contents above background levels (Richter and Kleitler, 1993; Gaye, 2001). Generally, groundwater is considered safe and viable in comparison to untreated surface water. However, high salt-loads contaminate the groundwater resources. The high salt-loads are caused by increases in chemical constituents and chemical contents (Total Dissolved Solids (TDS)) in groundwater, through the process called groundwater salinisation (Monjerezi, 2012). The salinisation of groundwater has water quality effects and results in the limitation of water for the intended uses. This affects communities dependent on groundwater both for domestic, agricultural as well as for industrial purposes. Additionally, salinisation enhances the mobilisation of potentially toxic minor elements in groundwater by forming metal-chloride complexes that are deteriorating to human health (Giordano, 2000; Bäckström et al., 2004). Arid and semi-arid environments are affected worse by the salinisation problem, as they have limited or no available surface water and solely depend on groundwater. However, studies suggest that no climatic zone in the world is free from salinisation (Rengasamy, 2006). The quality of the groundwater needs to meet local and international guidelines, to determine their fitness for the intended usage (WHO, 2006). In areas where salinisation of groundwater is occurring, it is necessary to identify the source(s) and mechanism(s) of salinisation for water management and salinity remediation purposes.

Salinisation affects both shallow and deep aquifers of the groundwater system, with the salt concentration in the aquifers dependent on the salt sources. Generally, shallow aquifers contain fresh groundwater as compared to the deeper aquifers (Van Weert et al., 2009). This is because shallow aquifers are most actively involved in the water cycle, and are recharged by recent fresh rainwater. But cases appear where the shallow groundwaters are saline, with the salts of natural or anthropogenic origin. Aquifers at deeper depth are at stagnant conditions and may have been there for thousands and millions of years. The dissolution of minerals from the rocks to the groundwater with time results in mineral enrichment in the water (Van Weert et al., 2009). Therefore, groundwater salinity mostly increases with increasing depth. Equally, not all deep aquifers are saline. Deep aquifers that are recently recharged contain fresh water.

In South Africa, salinity in shallow aquifers is prominent in the alluvial aquifers of both ephemeral and perennial rivers. The Berg River (a perennial river) of the Western Cape Province is one of these rivers, having the groundwater salinisation linked to long term irrigations on the semi-arid soils (le Roux et al., 2007). Studies on the Sandpruit River, which is a tributary to the Berg River, also report groundwater salinisation resulting from dryland agriculture (Flugel, 1991). Shallow aquifers salinisation in South Africa is more dominant in active agricultural regions, with the salinity coming from irrigation. However the Buffels River in Namaqualand, Northern Cape Province has intensive groundwater salinisation, but is located in a less agricultural active region. Instead of dominant agricultural activities, the Namaqualand region has been subjected to medium to small scale copper

and diamond mining activities. These mining activities are along the river bed, with the diamond mining concentrated at the coastal region towards Kleinzee. The Spektakel copper mine at Buffelsrivier and the Kleinzee De Beers diamond mine at Kleinzee are the main mining activities, with numerous small scale diamond mines along the river. Farming with sheep and goats as well as small scale irrigations along the river are also prevailing in the region.

Groundwater salinity in Namaqualand has been reported by several researchers, (Titus et al., 2000, 2002; Adams et al., 2004; Fersch, 2007; Pietersen et al. 2009; Benito et al., 2010, 2011; Leshomo et al., 2011) and this has deteriorated the water quality. The salinity dates back in history, with the mining activities at Spektakel Mine in the early 1970's reporting high salt loads in the groundwater abstracted from the alluvial Spektakel Aquifer of the Buffels River (Marais, 1981). Both shallow and deep aquifers in Namaqualand have high salt contents, with deep aquifers more saline as compared to the shallow aquifers (Titus et al., 2002 and Adams et al., 2004). The source(s) of salinity in Namaqualand are debatable; with previous studies suggesting the salts have natural origins (Leshomo, 2011). The salinisation is also attributed to high evaporation rates in the region, which concentrate the dissolved constituents (Titus et al., 2002; Benito et al., 2010). The Na-Cl rainwater type of the region and the preferential dissolution of evaporitic salts from shallow soils during infiltration have also been reported to cause salinity (Adams et al., 2004). Additionally, saline basement inflow into the fresh shallow aquifers has also been indicated (Benito et al., 2010).

However, the origin of the salts to the groundwater is still not fully understood. The possibility of seawater intrusion due to the close proximities of the aquifers to the coast has not been looked into. The local geology comprises of granites and gneisses and the contribution of these to salinity has not been investigated. The effects of small scale mining and the agricultural activities on the groundwater salinity are also not understood. Therefore, this study will focus on determining factors controlling high salt contents in the alluvial aquifers lining the Buffels River. This study will incorporate the recharge studies as well as the salinity sources studies as part of the qualitative water resources study to the alluvial aquifers of the Buffels River.

## **1.2 Problem Statement**

Groundwater salinity is a major problem in Namaqualand. In addition to the water scarcity problem, as the region is semi-arid to arid, the available groundwater resources have high salt-load contents and at some localities, evaporitic salts are evident on soil surface. High salt-loads have deteriorated the groundwater quality, and resulted in the limitation of the groundwater uses in the region. The source(s) of this salt is not known, and therefore difficult to mitigate. Identifying them is important for the groundwater resource management of the region. This will be important in ensuring the communities in the semi-arid to arid Namaqualand are supplied with sufficient water of good quality.

### 1.3 Aims and Objectives

The key aim of this study is to detect sources and mechanisms of salinity to the alluvial aquifers along the Buffels River. The study will further quantify the recharge rates to the aquifers. In attaining this, the following objectives and key questions have been set up:

**Key Objective 1:** To determine the origin of salinity in the alluvial aquifers lining the Buffels River

1. What are the dominant water constituents in the groundwater of the alluvial aquifers (the water type)?
2. What are the possible sources of salts causing the salinisation of groundwater to values above those contributed by precipitation and the possible salinisation mechanisms?
3. What are the potential remediation strategies for reducing the salts concentrations, centred on the identified salinisation processes identified in 2?

**Key Objective 2:** To determine recharge rates to the alluvial aquifers lining the Buffels River

1. What is the recharge rate to the alluvial aquifers based on the Chloride Mass Balance Calculations?
2. What are the possible recharge mechanisms to the alluvial aquifers?
3. What are the geochemical characteristics of precipitation in the Buffels River Catchment?

**Key Objective 3:** To detect how recharge influences the salinisation processes of the shallow alluvial aquifers of the Buffels River

1. How is the groundwater quality in recently recharged areas?
2. What is the influence of recharge mechanisms on the groundwater salinity?
3. What is the relationship between the groundwater salinity and recharge rates in the Buffels River Catchment?

### 1.4 Overview of Groundwater Salinisation

Salinisation is a global problem, and approximately 7% of the world's total land has high salt-loads (Rose, 2004). Salinisation is defined as a process of increasing chemical constituents as well as overall chemical contents (Total Dissolved Solids (TDS)) in water to values above background levels (Monjerezi, 2012). The high salt-loads in water deteriorate the water quality, limiting the suitability of water for the intended uses. A good understanding of the origins and mechanisms of salinisation is significant for the groundwater quality management. Different classifications are applied in ranking water resources based on salinity levels (Carpenter et al., 1974; Carpenter, 1978; Freeze and Cherry, 1979). The classifications differ in class names, used value limits and the parameters used. The classification of Freeze and Cherry (1979), is used in this study (Table). Since EC is measured directly in the field than TDS, EC values are used in the study as an estimate of the TDS concentration based on the formula:

$$TDS \left( \frac{mg}{l} \right) = EC (mS/m @ 25^{\circ}C) \times 6.5$$

### **1.4.1 Types of Salinity**

There are two different types of salinity, which are categorised depending on how salt is mobilised and where it is moved to. These are the primary and secondary salinity types as discussed below:

#### *1.4.1.1 Primary Salinity*

Primary salinity occurs naturally in water, and it is caused by the natural processes that have an effect on soil and water. This occurs generally in environments with high evapotranspiration rates and insufficient rainfalls (McDowell, 2008; Bridgman et al., 2008). The low rainfalls and high evapotranspiration rate conditions decrease the volume of water and increase salt concentrations in the groundwater. Semi-arid and arid environments are subject to potential primary salinisation due to their low rainfall and high evaporation rate.

#### *1.4.1.2 Secondary Salinity*

Secondary salinity results from human activities that cause changes to the hydrological cycle. The changes mainly occur in agricultural and environmental activities environments. Characteristic of the secondary salinity types is that they are localised. These include:

##### (a) Dryland Salinity

Dryland salinity is common in areas where deep-rooted perennial vegetation are replaced by crops and pastures that have shallow root systems in non-irrigated areas (Scanlon et al., 2002). The crops use less water, and cause a decrease in annual evapotranspiration as well as an increase in recharge to the water table. Recharge causes water table rises and mobilisation of salts stored deep in the soils, resulting in the salinisation of groundwater. Dryland salinity may also be caused by the exposure of natural saline soils and sodic soils (Phillips et al., 2003). These cause poor soil structures and reduce water infiltrations resulting in minimal leaching of salts below the root zone.

##### (b) Irrigation Salinity

Irrigation water can infiltrate through the non-saturated zone and reach the water table. This results in a localised rise of the groundwater level. The risen water levels dissolve the soil salts, causing the salinisation of groundwater. The rise in the water table further cause direct evaporation from the shallow water table, which further increases the salinity concentration in groundwater (Van Weert et al., 2009). This is the most common form of secondary salinisation (Ghassemi et al., 1995).

(c) Urban Salinity

This is groundwater salinisation in the urban areas, generally caused by urban development activities (Slinger and Tenison, 2007). Urban activities such as over-watering of parks and leaking pipes result in groundwater rises. The rising groundwater mobilises the salts in the landscape, and redistribute it into the near soil surface and water causing salinisation. In addition to the natural occurring salts, urban environments have other anthropogenic salt sources such as sewages and salts contained in building materials.

(d) Industrial Salinity

The industrial processes; such as mining activities concentrate salts in their industrial waste water. If not handled well, the saline waste water leaks to the groundwater and cause salinisation. Early mining activities undertaken before mining environmental regulations were put in place resulted in the abandoned mines being the sources of salts to the water resources (Hohne and Hansen, 2008).

### **1.4.2 Sources of Salts**

Groundwater salinity results from the addition of solutes to the groundwater and from concentration processes of dissolved constituents through evapotranspiration (Phillips et al., 2003). The solute sources can be of natural origin, (i.e. from the solution of halites and seawater intrusions) or of secondary origin (i.e. from the anthropogenic activities). The different causes of salinity are differentiated based on their chemical composition. The sodium and chloride salts dominate in many saline water of the world, but salts of other ions such as calcium, magnesium, sulphate and bicarbonate are also found in specific locations (Rengasamy, 2006).

#### *1.4.2.1 Rainfall (Cyclist Salt)*

Rainwater contains low amounts of salt, which is included in water evaporated from the oceans and deposited over the coastal areas. These are mainly Na-Cl salts, due to the high sodium and chloride ions in seawater. Over time, the salts deposited by rain accumulate in the landscape and is concentrated by evaporation. This is dissolved by recharge water, causing salinisation of the groundwater (Rengasamy, 2006). Furthermore, precipitation interacts with atmospheric gases and particles increasing the salt concentration in the precipitation water (Richter and Kreitler, 1993).

#### *1.4.2.2 Marine Salts*

Salinity originating from marine can be from the connate saline groundwater, marine transgressions, incidental seawater flooding, seawater intrusions and seawater sprays (Hudak, 2000; Vengosh et al., 2002). These have been discussed below:

(a) Connate Saline Groundwater

The connate saline groundwaters are common in sedimentary formations of marine origin, where sediments were deposited in seawater and it is still trapped between the soil particles (interstices) (Van Weert, 2009). The recent precipitations flush out the trapped seawater into the groundwater. This is common in aquifers with the sedimentary formations of marine origin. Connate saline waters are prevailing in deep aquifers as precipitation in shallow aquifers flushes out the formational water (Monjerezi, 2012). Therefore for groundwater of a connate salinity origin, salinity increases with depth below land surface as chemical reactions with aquifer material, resident time, and mixing of different waters increase (Vengosh et al., 2002).

(b) Seawater Intrusion (Ingress)

Seawater intrusions are common in coastal aquifers, deteriorating the water quality in the aquifers. Seawater intrusions are caused by changes in hydraulic heads, as the coastal aquifers are hydraulically connected to the sea (Wicks et al., 1995; Wicks and Herman, 1996; Park et al., 2005). Over abstraction of aquifers causes a decrease in the hydraulic head, and result in the up-coning of saline seawater to fill the aquifers (Vengosh et al., 2002; Kim et al., 2003). Under natural conditions, groundwater in coastal aquifers flow towards the sea. Over pumping of the coastal aquifers cause a decrease in the fresh water heads as compared to the sea water heads and this result in sea water intrusion (Carreira et al., 2014).

(c) Marine Transgression and Incidental Flooding

These are caused by natural sea level changes over geological times, with the occurring of transgressions and regressions. Coastal lowlands become flooded by the sea during the marine transgression periods (Hanor and Evans, 1988). This process takes a long time, before a regression period occurs, causing salinisation of the coastal aquifers. In addition to this, incidental seawater flooding, which occurs over a short time (i.e. during tsunamis), are common in coastal areas also causing salinisation of the aquifers.

*1.4.2.3 Natural Terrestrial Salts*

This includes the salinisation caused by the concentration of mineral contents by evaporation, solute sources from the dissolution of evaporites and subsurface salts as well as salts produced by salt filtering membranes and recent igneous activities.

(a) Evaporation at or near Land Surface

Evaporation causes salinity by concentrating the dissolved constituents' in the residual water. Evaporation is a significant groundwater salinisation process in arid and semi-arid regions, where the evaporation rates exceeds precipitation amounts resulting in no/less flushing of accumulated salts

(Deverel and Gallanthine, 1989; Yechieli and Wood, 2002). The saline groundwaters concentrated by evaporation are prominent in shallow aquifers as compared to the deeper aquifers.

(b) Dissolution of Naturally Occurring Soluble Minerals

The dissolution of evaporite minerals on the surface and the un-saturated zone of the sedimentary basins by recharging water results in the salinisation of groundwater. Many sedimentary basins contain evaporites at great depths, and these may be dissolved either by regional or local groundwater recharges (Bennet and Hanor, 1987; Macpherson, 1992). The dissolution of soluble salts such as gypsum and halite minerals within the aquifer leads to gradual increase in salinity and the chemical modification toward predominance of the dominant ions (Herczeg et al., 2001). The salts are flushed into the groundwater by the seasonal pulses of recharge may, and in the process the flowing water can also dissolve any other salts of the aquifer materials.

(c) Aeolian Deposits

Wind-blown sea-salts aerosols also cause salinisation of soil surfaces and surface water. The infiltrating water flushes these salts to the groundwater. The strong winds also carry mineral matter and solution droplets in the atmosphere, and these are dissolved in precipitation and recharged to the groundwater (Richter and Kreitler, 1993).

(d) Geological Sources

The lithological make-up of the aquifer can also contribute to the salinisation of groundwater. The compacted layers of clay or shale in the sedimentary basins turn out to be filtering membranes (geological membranes), sieving out the dissolved large ions in the percolating groundwater (Whitworth and Fritz, 1994). These result in the salinisation of groundwater at this lithology. In addition to the sedimentary formations, saline water can be of geothermal origin where saline fluid inclusions in the minerals of hydrothermal, metamorphic, or igneous origin becomes part of the groundwater (Richter and Kreitler, 1993). The weathering of the aquifers also mobilise ions and these are dissolved in the groundwater. For deeper aquifers, with long residence times the water-rock interactions dissolve the ions out of the aquifers causing the salinisation of groundwater.

*1.4.2.4 Anthropogenic Salts*

These are human activities (anthropogenic pollution) such as road salt; domestic, industrial and agricultural waste water; spilled oil and gas field brines and brines from desalination plants that result in the addition of salt-loads to the groundwater when they are infiltrated. The anthropogenic salt sources are differentiated from others in that they usually result in localised salinisation of groundwater. The shallow and high permeability characters of the alluvial aquifers subject them to anthropogenic salt sources.

### 1.4.3 Tracers of Salinity Sources

There are multiple salinity sources to the groundwater (discussed above), and this makes it difficult to identifying the salinity sources (Richter and Kleitler, 1993; Vengosh, 2005). There are unique and distinctive chemical and isotopic compositions characteristic of each salinity source and these are used as fingerprints in tracing the salinity sources. It is assumed that the chemical and isotopic compositions (fingerprints) of the original saline sources are preserved (Monjerezi, 2012). However, water-rock interactions modify the original compositions of the saline sources and mask its identity. The combination of geochemical and isotopic tracers provides information that is useful in resolving the multiple salinity sources. Different conservative chemical and isotopic tracers are therefore used to distinguish between the different salinity sources. The reason for the salinity study mostly predominate which salinity tracer to use (Monjerezi, 2012). The parameters mostly used include major and minor ions (i.e.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Br}^-$ ) and some isotopes (i.e.  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ).

#### 1.4.3.1 Geochemical Tracers

Several ratios of major and minor groundwater constituents such as  $\text{Br}^-/\text{Cl}^-$ ,  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Mg}^{2+}/\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-/\text{NO}_3^-$  are used to distinguish between the major sources of salinity. These ratios have been illustrated in several groundwater salinity studies i.e. Edmunds (1996), Palmer and Swihart (1996), Davis et al. (1998), Marie and Vengosh, 2001; Panno et al., 2006 and Alcalá and Custodio (2008). In addition to the ratios, the chemical constituents are also used in tracing the sources of salt-loads to the groundwater (Richter and Kreitler, 1993). The most common used chemical constituents are: Na, Ca, Mg, Cl,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ . The elements occur in distinct ratios distinctive of their salinity sources and are used in the differentiation of the salinity sources (Richter and Kleitler, 1993). These ratios work best as tracers when there is minimal influence of geochemical reactions, after the mixing of saline and fresh groundwater (Monjerezi, 2012). They are therefore useful in groundwater with high salt-loads (Richter and Kleitler, 1993). The use of conservative constituents such as chloride and bromide in salinity source studies is also common.

#### 1.4.3.2 Isotope Tracers

Several environmental isotopes such as  $\delta^{11}\text{B}$ ,  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^{36}\text{Cl}/\text{Cl}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  are used in salinity source studies (Palmer and Swihart, 1996; Phillips, 2000; Rao et al, 2005). The  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  stable isotopes are commonly used in the determination of saline and fresh groundwater mixing relationship and in assessing the effects of evaporation on groundwater (Davisson and Criss, 1996; Yechieli et al., 2001). These isotopes are further used in differentiating remnants of diluted evaporated seawater, formation water and meteoric fallout from seawater intrusions (Herczeg et al., 2001). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes are used to trace salinisation by agricultural return flow (Bolke and Horan, 2000). In addition,  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes are further used in tracing the strontium sources to the groundwater, weathering processes, flow paths as well as the groundwater mixing in a catchment

(Armstrong et al., 1998; Vengosh et al., 1999).  $^{36}\text{Cl}/\text{Cl}$  is used to differentiate saline sources of meteoric source (of seawater origin), from other saline sources that have low  $^{36}\text{Cl}/\text{Cl}$  ratios (Phillips, 2000).

$^{36}\text{Cl}$  is an unstable isotope produced in the atmosphere, in near-surface rocks as well as in the deep subsurface. In the Earth's atmosphere,  $^{36}\text{Cl}$  is produced cosmogenically by the proton induced spallation of stratospheric  $^{40}\text{Ar}$  and by neutron activation of tropospheric  $^{36}\text{Ar}$ . Minor amounts of  $^{36}\text{Cl}$  are also produced at the Earth's surface by spallation of potassium and calcium, as well as in the subsurface through the capturing of neutrons produced by U and Th decay by  $^{35}\text{Cl}$ . The nuclear testing of 1950s-1960s also produced significant  $^{36}\text{Cl}$ . The main advantages to the use of  $^{36}\text{Cl}$  as a groundwater tracer are its dating range (up to approximately 1.5 Ma, an age range not covered by other isotopes) and the common presence of chlorine isotopes in groundwater.

Potential sources for the observed levels of  $^{36}\text{Cl}$  and chloride concentrations in Namaqualand include meteoric recharge; anthropogenic sources, the ancient evaporation contributions; ancient seawater trapped in rocks; evaporate dissolution; and water/rock interactions with  $^{36}\text{Cl}$  and chloride primarily coming from subsurface rock leaching. The equilibrium  $^{36}\text{Cl}/\text{Cl}$  value will depend on the rate of production of  $^{36}\text{Cl}$ , which is a function of the U and Th concentrations in the aquifer. Ratios higher than  $10^{-12}$  in natural waters indicate the presence of thermonuclear  $^{36}\text{Cl}$ ; maximum global values during sea-level atmospheric nuclear weapon tests were on the order of  $10^{-11}$ . Thermonuclear  $^{36}\text{Cl}$  is likely to become more frequently used as an indicator of young water as the thermonuclear  $^3\text{H}$  in ground water decays to background levels over the next couple decades.  $^{36}\text{Cl}$  is used as a tracer of salt sources and their transport in groundwater (Cresswell et al., 1999). The stable chlorine isotopes in the atmosphere shows an exponential decay with distance from the coast and coupled with the  $^{36}\text{Cl}$  latitudinal effects determines the  $^{36}\text{Cl}/\text{Cl}$  ratios (Keywood et al. 1997; Cresswell et al., 1999).

#### 1.4.3.3 Tracers of Salinity in this Study

The combination of geochemical and isotopic tracers was used in determining the sources of salinity to the alluvial aquifers of the Buffels River. The ratios of major ions such as  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Mg}^{2+}/\text{Ca}^{2+}$  as well as  $\text{Ca}^{2+}/\text{Sr}^{2+}$  were used with the stable isotopes of oxygen ( $^{18}\text{O}$ ) and hydrogen ( $^2\text{H}$ ). Radioactive isotopes of  $^3\text{H}$  as well as the  $^{36}\text{Cl}/\text{Cl}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the groundwater samples were also used in detecting the sources of mineralisation to the groundwater. In addition to these, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes of the Spektakel Suite which comprises the basement rocks along the Buffels River catchment were used as a baseline.

### 1.5 Overview of Groundwater Recharge

The water balance components of the groundwater system comprises of the recharges, discharges as well as the changes in storage (Freeze and Cherry, 1979). Groundwater recharge is defined as the portion of infiltrating water that is added to the groundwater system, and reaches the saturated zone made available at the water table forming an addition to the groundwater reservoir (Mazor, 1990).

Groundwater recharge is an important component of the water balance for it quantifies the inputs to the groundwater. This is important for sustainable management of water resources, control of subsurface contamination, and better understanding of hydrologic and ecological variability (Ng et al., 2009). Recharge studies are therefore done for both water quantity and quality purposes.

Recharge studies are essential in arid and semi-arid regions as the population in these regions merely depend on groundwater for their domestic, agricultural and industrial activities. Groundwater is also prone to depletion in these regions as it is mostly the only water source (de Vries and Simmers, 2002). However the estimation of recharge is difficult in arid and semi-arid environments as there are high evaporation rates than precipitation (Ng et al., 2009). Furthermore, there are large recharge variations (both temporal and spatial) in the arid and semi-arid regions as compared to other climatic regions. There is also lack of hydrological data from these regions, as they are mostly remote hence no historical recharge studies are available. Therefore, groundwater recharge in semi-arid and arid environments depend on rainfall events of high concentration, accumulation of rain water in depressions and streams, and the ability of rain water to escape evapotranspiration by rapid percolation through cracks, fissures, or solution channels.

Recharge processes to the groundwater are affected by the hydro-geologic environments which comprise of the geomorphology (topography, soil and vegetation), geology and climate (Scanlon et al., 2002 and Ng et al., 2009). The hydro-geologic environments interact to create the distinctive conditions that result in recharge to the groundwater. These hydro-geologic factors therefore influence the choice of the recharge estimation method. Vegetation cover is of great importance in determining recharge potential at a specific site, with high recharge rates at non-vegetated areas as compared to the vegetated areas (Gee et al., 1994). However, in the tropics where rain occurs as huge downpours, non-vegetated areas actually receive less recharge due to runoff (Simmers, 2002). There occurs substantial retardation of the rain water in vegetated areas; thereby increasing the recharge to the aquifer. The impact of vegetation was further indicated in Australia where deep rooted trees and shrubs were replaced by shallow rooted crops resulting in recharge increases (Allison et al., 1990). Coarse grained soils generally results in higher recharge as compared to the fine grained soils.

### **1.5.1 Groundwater Recharge Mechanisms**

Rainwater and snow are the main sources of recharge to a groundwater system. Recharge mechanisms from these sources can either be direct or indirect (Lerner et al., 1990). Direct recharge occurs by direct vertical percolation of water in excess of soil moisture deficits and evapotranspiration through the vadose zone to the groundwater (Ng et al., 2009). Indirect recharge occurs by the delayed percolation of water that is subjected to evapotranspiration. Indirect recharge results in enriched or depleted groundwater isotopes in comparison to the precipitation isotopes. Indirect recharge is prevailing in arid and semi-arid environments, but direct recharge mechanisms can still have significant impact on the overall groundwater budget (Kearns and Hendrickx, 1998). Nevertheless, direct recharge in these environments occurs episodically (Ng et al., 2009).

Furthermore, indirect recharge result in groundwater typically enriched or depleted in isotopes in comparison to precipitation. Differences exist between the recharge mechanisms for the shallow and deeper aquifers.

#### *1.5.1.1 Shallow Aquifer Systems*

Shallow aquifers are mostly recharged by the direct infiltration of precipitation, reaching the shallow water tables. The recharge rates in these aquifers are limited by the ability of the aquifers to store and transmit water. These aquifers are mostly unconfined, and are susceptible to contamination.

#### *1.5.1.2 Deep Aquifer Systems*

Deeper aquifers are recharged by transmission of water along faults and cracks as well as by losses from the overlying shallow aquifers (Scanlon et al., 2002). Most deep aquifers are confined and occur at stagnant conditions at deeper depths as they are not replenished by recent recharged water and may have been there for thousand and million years (Van Weert et al., 2009).

#### *1.5.1.3 Arid and Semi-Arid Environments*

Although the rainfall amounts in arid and semi-arid environments are low, groundwater recharge still takes place. Groundwater in arid and semi-arid regions is mostly recharged by indirect recharge processes, with the infiltration of water from the ephemeral streams (Lerner et al., 1990 and de Vries and Simmers, 2002). Recharge in the alluvial valleys occurs in the topographic lows i.e. in channels of ephemeral streams (Scanlon et al., 2002). The recharge rates in the arid and semi-arid regions are limited by the availability of water which is mainly controlled by climatic factors such as precipitation and evapotranspiration (Scanlon et al., 2002).

### **1.5.2 Methods for Estimating Groundwater Recharge**

Different methods exist for estimating recharge to the groundwater (Gee and Hillel, 1988; Simmers 1988, 1997; Lerner et al., 1990; Allison et al., 1994). These have been divided into physical, chemical and numerical methods. The objective of the recharge study determines the recharge estimation method to be used and indicates the temporal and spatial scales of the recharge estimates (Scanlon et al., 2002). The study environment and the availability of required data for a specific technique also determines the method to be used in recharge estimation. There are uncertainties in each recharge estimating approach, and the application of multiple techniques help reducing this. Recharge studies done for water resource evaluation goals require large spatial and temporal scales while the recharge studies for water quality purposes are done on small spatial scales as they need to be detailed (Scanlon et al., 2002). The different methods are discussed below:

### 1.5.2.1 Physical Techniques

Physical methods (i.e. lysimeters, water balances, measurements of soil water fluxes and water table fluctuations) use soil physics to estimate recharge by measuring hydrological parameters. These methods are more effective in wet regions, where fluxes are high and changes in hydrological parameters low (Allison et al., 1994). In arid and semi-arid environments, the physical methods are prone to errors, because they only measure recharge at specific moments and/or locations, from which spatial and temporal extrapolations must be made (Lerner et al., 1990).

#### (a) Water Table Fluctuation (WTF)

The method is based on the principle that the risings of groundwater tables in the unconfined aquifers are a result of water recharging the water table (Scanlon et al., 2002). Generally, this method requires shallow water tables and is better applied over short time periods (Healy and Cook, 2002). Recharge is calculated using:

$$R = S_y \times \frac{dh}{dt} \text{ (After Scanlon et al., 2002)}$$

Where  $S_y$  is the specific yield,  $h$  is the water table height and  $t$  is time. In using this method, uncertainties has been reported in determining a representative specific yield and ensuring the fluctuations in the water levels are due to recharge and not a result of other factors such as changes in atmospheric pressure (Scanlon et al., 2002).

#### (b) Darcy's Law

Darcy's law is used in estimating cross-sectional flows in the saturated zone. The method assumes steady flow conditions and no water extractions from the aquifers. Recharge is calculated from:

$$R = \frac{qA}{S}$$

Where  $q$  is the sub-surface water flux,  $A$  is the cross-sectional area and  $S$  is the surface area that contributes to recharge. The method has an advantage that they represent the actual flow conditions. The recharge estimates based on Darcy's law have high uncertainties due to high variability's of hydraulic conductivity (Scanlon et al., 2002).

#### (c) Lysimeter

Lysimeters are used to study the interactions between the atmosphere, soil, water and plants under natural or artificial conditions (Healy, 2010). The lysimeters are installed at depth to limit the influence of surface processes (Lerner et al., 1990). These are used in recharge studies by measuring the rate of water drainage out of the bottom of the lysimeter. The process directly measures balance

components, but there are limitations on the applicability of the method to catchments with identical features (Simmers, 1997).

### 1.5.2.2 Chemical Techniques

Chemical recharge estimation methods are based on the distribution of a tracer, with  $^2\text{H}$ ,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{18}\text{O}$  and Cl being the most common. They have an advantage over physical methods of representing a spatially uniform input to the groundwater system and are cost effective (Allison, 1987; Lerner et al., 1990). They are therefore favoured in arid and semi-arid environments (Gee and Hillel, 1988; Allison et al., 1994).

#### (a) Event Markers

Event markers such as bomb-pulse tritium are effective in estimating recharge to the groundwater (Allison et al., 1994). Additionally chlorofluorocarbons (CFCs) and tritium /helium-3 ( $^3\text{H}/^3\text{He}$ ) are also used in recharge estimates.  $^3\text{H}/^3\text{He}$  is used in estimating recharge rates, where groundwater flow is vertical (Scanlon et al., 2002). The type of tracer used depends on the mean residence time of the aquifer. The recharge rate is therefore determined by dating water at several points in a vertical profile and calculating the groundwater velocity by inverting the age gradient, extrapolating the velocity to the water table if it is not measured near the water table and multiplying the velocity by the porosity for the depth interval (Cook and Solomon 1997).

$$R = \frac{dz}{dt} \times \theta$$

Where  $z$  is the depth,  $t$  is time and  $\theta$  is volumetric water content. . These require hydrogeological investigations and hydrochemical analyses (Walker et al., 2002).

#### (b) Environment Tracers

Tracer (isotopic) techniques uses water soluble natural tracers (e.g.  $^{36}\text{Cl}$ ,  $^{18}\text{O}$ ,  $^2\text{H}$  and Cl) and artificial applied tracers (e.g. bromide and tritium) to estimate recharge (Allison et al., 1994). The choosing of the type of tracer to be used depends on the recharge rates, having artificial tracers useful at high rates  $>100\text{mm}$  and the chloride tracer over the range (Scanlon et al., 2002). These are effective in estimating recharge in arid and semi-arid regions. Though convenient and sometimes the only available method for arid areas, tracer methods suffer the handicap of mass distortions from secondary inputs and mixing and/or dual flow mechanisms (De Vries et al., 2000).

Chloride is a natural tracer and has an advantage of being popular due to its universal availability and high sensitivity at lower recharge rates (Ng, et al., 2009). The chloride mass balance method (CMB) (Eriksson and Khunakasem, 1969) is used in recharge estimation in this study. The CMB approach assumes the average rate of chloride deposited in precipitation equals the average rate of chloride

flushed out of the unsaturated zone (Scanlon et al., 2002). The method further assumes that chloride is conservative in the groundwater system and steady-state conditions are maintained with respect to long-term precipitation and chloride concentration in that precipitation. In South Africa, the recharge rates estimated from groundwater chloride concentrations range from 0 to 8 mm/year (Sami and Hughes, 1996). This uses a general equation of:

$$R = \frac{(P \times Cl_p)}{Cl_{gw}}$$

Where R: recharge rate (mm/a),  $Cl_p$ : Chloride concentration in rainwater and  $Cl_{gw}$ : Chloride concentration in groundwater

### *1.5.2.3 Numerical Models*

The numerical models predict recharge rates from available hydraulic information (Scanlon et al., 2002). The models are reliant on the water budget method which is based on the water budget equation. The hydraulic-conductivity data determines the reliability of the recharge estimates from numerical models. Due to the variations of hydraulic conductivity over several orders of magnitude, the estimation of recharge rates using model calibration may not be very accurate. The estimated recharge is therefore often non-unique as same distribution of hydraulic heads can be produced with a range of recharge rates (Scanlon et al., 2002). Gee and Hillel, (1988); Allison and others (1994) as well as Phillips, (1994) caution against their application in semiarid environments. Because diffuse recharge rates in such settings can be quite small relative to precipitation and evaporation, they are very sensitive to uncertain model parameterisations and input errors. For this reason, tracer-based recharge estimation methods are favoured by Gee and Hillel (1988) and Allison et al. (1994) in semiarid environments. Numerical methods usage in semi-arid regions has been warned against by earlier authors (Allison et al., 1994; Phillips, 1994). This was due to the small diffuse recharge rates in the semi-arid regions as compared to precipitation and evaporation which are sensitive to models and results in errors. Numerical modelling uses measured hydrological parameters to simulate numerical recharge estimations (Sanford, 2002). The acquisition of hydrological data required for the model has costs implications.

### **1.5.3 Estimation of Recharge in this Study**

The chloride mass balance method was used in estimating the recharge rates to the alluvial aquifers along the Buffels River. The equation used was that of the groundwater from the saturated zone. The recharge rates were determined on an annual basis, and is presented as mm/a. Furthermore, oxygen ( $^{18}\text{O}$ ) and hydrogen ( $^2\text{H}$ ) isotopes were used in determining the recharge mechanisms to the alluvial aquifers.

## 1.6 Study Area

This study was done on the alluvial aquifers of the Buffels River in the Namaqualand region of Northern Cape, South Africa to see the extent of salt-loads within the groundwater. The Buffels River, which is 250 km in length, is the largest ephemeral river in the Northern Cape Province. It drains an area of approximately 9250 km<sup>2</sup> from the Kamies Mountains and discharges into the Atlantic Ocean at Kleinsee (Fig. 1.1) (Benito et al, 2011). These alluvial aquifers are important as they are the leading water source for rural communities along the river (i.e. Buffelsrivier and Komaggas). Only big towns (e.g. Kleinsee) have access to piped water from the Orange River, the rest of the region depends on groundwater. The groundwater samples from these aquifers were accessed through existing boreholes, hand dug wells and shallow field augured wells (Fig. 1.2). The human population dependent on the Buffels River groundwater is estimated to fewer than 100 commercial livestock farms, roughly 250 communal livestock farmers and five communal villages along the basin comprising approximately 2,200 people (Benito et al., 2010). The groundwater samples were taken from the alluvial aquifers along the river, covering about a 100km stretch towards the coast. The highest sampling point was taken at the Buffels River-N7 national road crossing and the lowest sample taken at Kleinsee, before the river enters the Atlantic Ocean (Fig. 1.3).

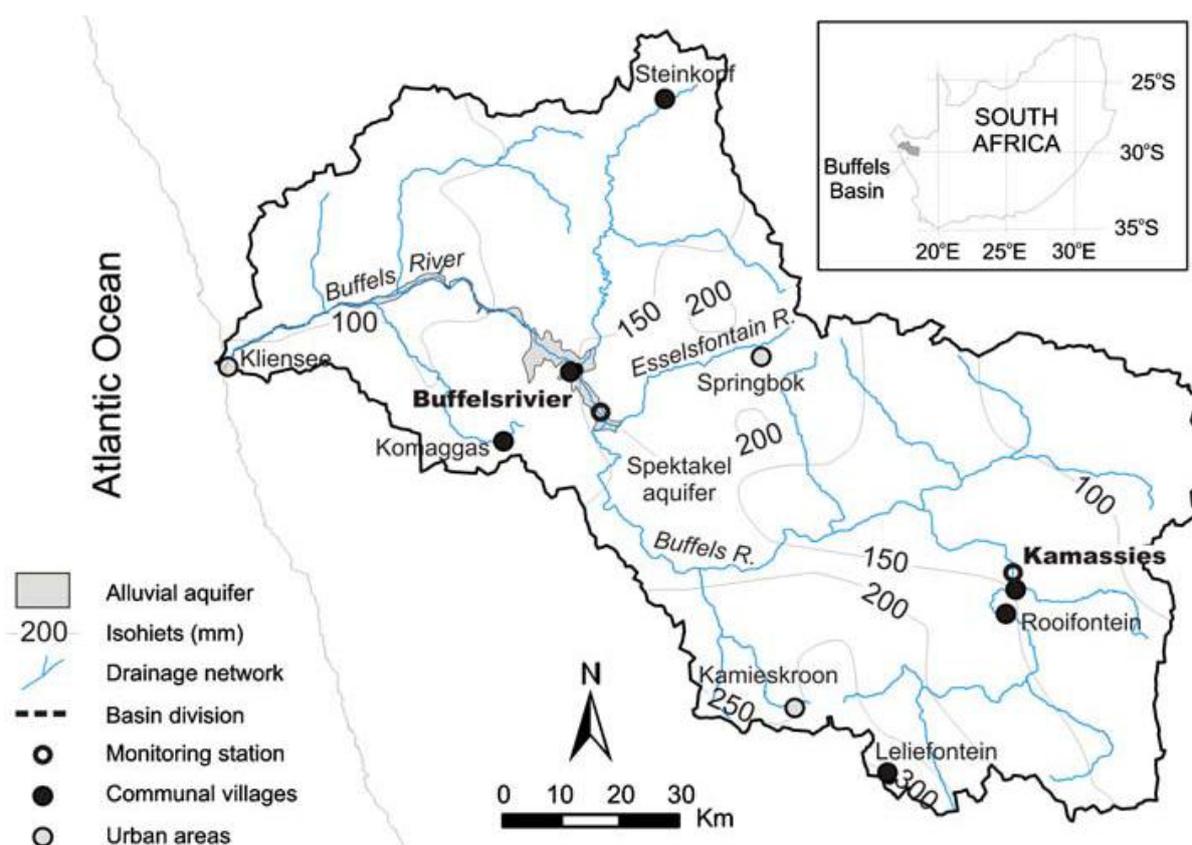
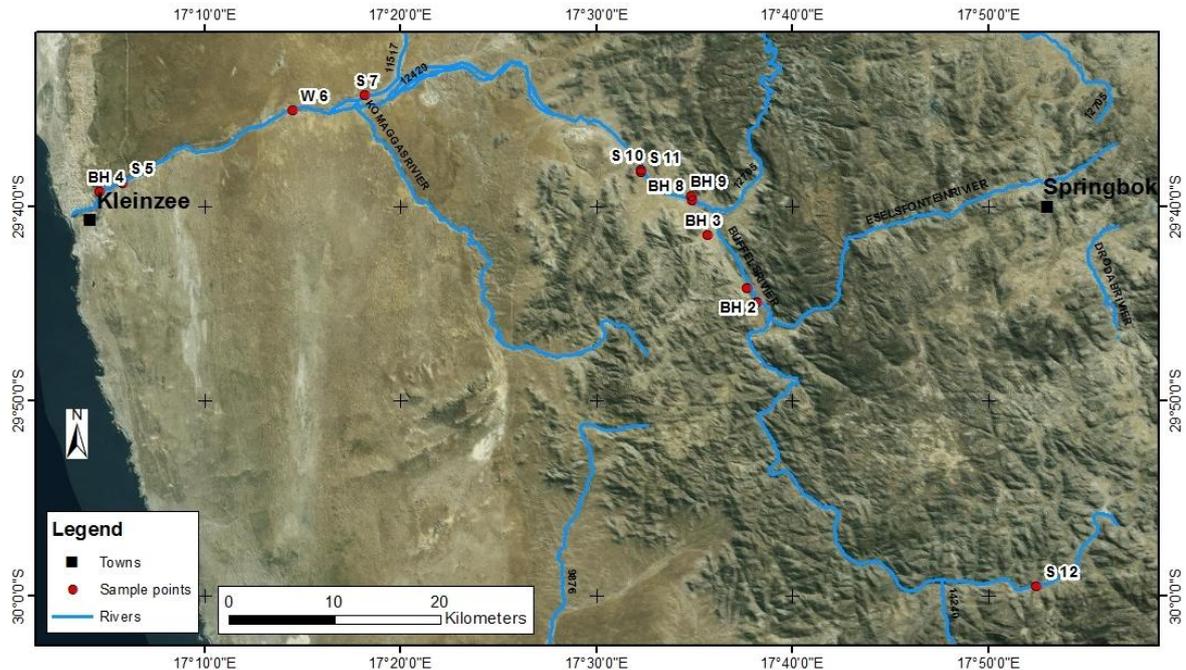


Figure 1.1: The Buffels River catchment area with the extent of the shallow alluvial aquifers indicated. Taken from Benito et al., 2010.



**Figure 1.2: Field photos of the sampling points (a) municipal supply borehole for the town of Buffelsrivier; (b) typical borehole with minimal protection and access pipe leading to an agricultural watering point near the town of Kleinzee; (c) shallow hand dug well in the middle of the Buffels River; and (d) shallow field augured hole in the middle of the Buffels River.**



**Figure 1.3: Distribution of groundwater sampling locations**

### 1.6.1 Geological Context

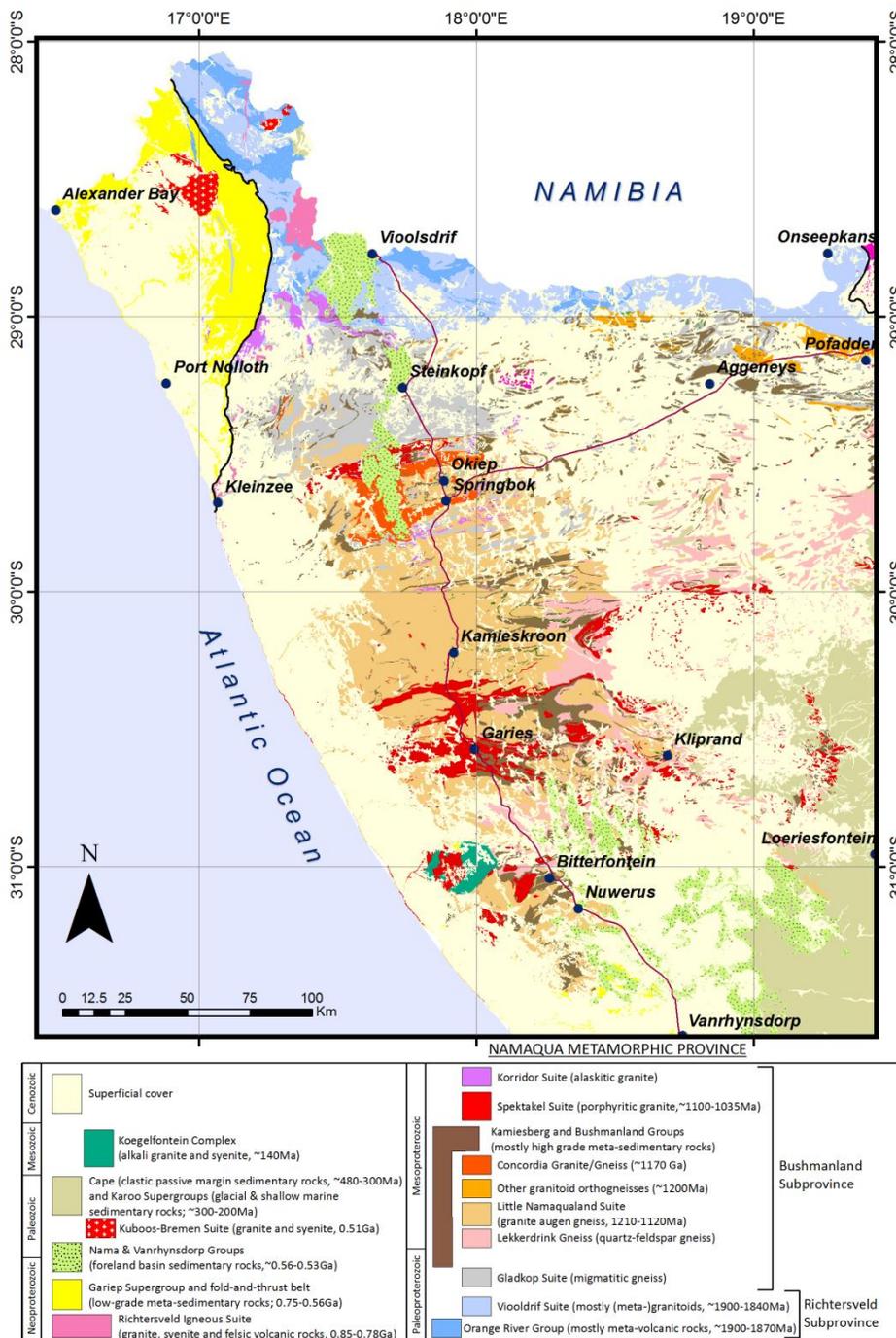
The Buffels River flows through the Mesoproterozoic Bushmanland Subprovince of the Namaqua-Natal Metamorphic Complex (NNMC). An overview of the geology of the entire Namaqualand region as well as that of Central Namaqualand, where the Buffels River is situated is described below:

#### 1.6.1.1 Regional Geological Overview

The geology of Namaqualand is subdivided into three geological provinces, namely the Namaqua Metamorphic Province (NMP), Gariiep Complex and the Phanerozoic Cratonic cover (Tankard et al., 1982; Visser, 1989). The NMP forms part of the larger Namaqua-Natal Belt of southern Africa. The Namaqua-Natal belt is one of the several 1.0–1.2 Ga orogenic belts understood to have been involved in the assembly of the Rodinia supercontinent (Dalziel et al., 2000). NMP represents a deformed and metamorphosed belt consisting of meta-sedimentary and meta-igneous rocks. The main lithological units in the Namaqua Province comprises of meta-volcano-sedimentary successions intruded by various granitoid intrusions (Blignault et al., 1983). The NMP rocks retain evidences of four metamorphic events (Robb et al., 1999; Clifford et al., 2004). The first metamorphism was of greenschist facies (D1), and this occurred during the Orange River Orogeny (1700-1900Ma) (Blignault et al., 1983). D2 and D3 metamorphisms occurred during the Namaquan Orogeny, dated at 1020-1220Ma (Robb et al., 1999; Clifford et al., 2004). D4 occurred after the Namaquan Orogeny, and is understood to be a result of tectonic relaxation (Thomas et al., 1994; 1996; Colliston and Schoch, 2003).

The NMP has been subdivided into several tectono-stratigraphic domains, which bounded by major shear zones. Tankard et al. (1982) divided it into Eastern, Central, and Western Zones, which Hartnady et al. (1985) subsequently re-named into the Bushmanland, Richtersveld, Gordonia and Kheis tectonic Subprovinces respectively. With the exception of the Richtersveld Subprovince, all these subprovinces experienced polyphase deformation, metamorphism, and voluminous plutonic activities during the Namaquan Cycle (-1200-1000 Ma) (Thomas et al., 1996). These subprovinces are sub-divided into terranes and are categorised based on marked changes in lithostratigraphy across structural discontinuities (Cornell et al., 2009). The Richtersveld Subprovince (ca 2000 Ma) is the northern boundary of the Namaqua Metamorphic Province and contains low to medium-grade supracrustal rocks and intrusions (Pettersson, 2008) (Fig. 1.4). It comprises of intrusive and volcanic rocks that underwent deformation and low- to intermediate-grade metamorphism (greenschist facies) during the late Kheisian 'Orange River Event' (Reid & Barton, 1983; Hartnady et al. 1985). The subprovince is subdivided into three terranes: the Pella Terrain in the east, the central low-grade Vioolsdrif Terrane and the Sperrgebiet Terrane in the west (Eglington, 2006).

The Bushmanland Subprovince forms the western continuation of the transcontinental Namaqua-Natal Metamorphic Province (Robb et al., 1999). It comprises of para- and orthogneisses, amphibolites, psammo-pelitic schists, quartzites, calc-silicate rocks and granitoids (Joubert, 1986). These rocks suffer the upper amphibolite to granulite metamorphic grade (Reid et al., 1997). The subprovince is divided into Aggeneys, Okiep, Steinkopf and Garies Terranes, which are separated by the Buffels River-Pytsberg thrust (Eglington, 2006). The Buffels River is located within the Bushmanland Subprovince (Clifford, 1970; Hoffman, 1992). The Gordonia Subprovince consists of high-grade metasedimentary and metavolcanic rocks, which are highly foliated (Reid et al., 1997). It is divided into the Kaaiberg, Kakamas and Areachap Terranes (Thomas et al., 1994). The three terranes are separated by the Bovenrug Shear Zone and the Hartebees River Thrust (Pettersson et al., 2007). The Kheis SubProvince is placed between Gordonia SubProvince and Kaapvaal Craton. It comprises of the arenitic metasediments (quartzites and phyllites) with very few amphibolites and volcanic rocks of the late Paleoproterozoic age (Moen, 1999). Kheis is characterised by the "thin-skinned" fold and thrust belts of medium to high metamorphism (Moen, 1999; Eglington, 2006). The subprovince has a high deformed geology, which is attributed to the collision between NMP and the Kaapvaal Craton (Van Niekerk, 2006 and Moen and Armstrong, 2008).



**Figure 1.4: Regional geology of the western Namaqualand outlining the broad geology of the Buffels River catchment. Map from the Council for Geosciences.**

1.6.1.2 Geology of the Buffels River

The Buffels River catchment bedrock comprises of impermeable meta-sedimentary rocks, basic granites and ultrabasic intrusive rocks (Marais et al, 2001). These are cut by the basement faults resulting from the tectonics. The catchment is mainly characterised by granites and gneisses. These

are underlain by Proterozoic crystalline basement rocks of the Namaqua Metamorphic Province (Clifford et al., 2004). To the north of the Buffels River catchment, Nama Group cover rocks overlay the basement rock. To the north-west of the region the basement rocks are obscured by Gariep Complex cover rocks and by Cenozoic surficial sediments to the east and west of the region (Joubert, 1986). In south of the Buffels River catchment, Nama Group, Cape Supergroup and the lowermost units of the Karoo Supergroup cover rocks obscure the Namaqua Province basement rocks (Albat, 1984). The younger sediments are characterised by alluvium, pan sediments, calcareous soil, red Aeolian sand and superficial cover sand.



**Figure 1.5: View down the Buffels River catchment from the top escarpment at the town of Buffelsrivier looking west towards the coast.**

### **1.6.2 Geomorphology**

Namaqualand consists of flat flood plains, escarpment and the plateau. The topography varies from a very low altitude and relief coastal zone to a high altitude escarpment zone (Fig. 1.5). Namaqualand is characterised by three geomorphologic regions, namely the coastal lowland, an escarpment zone and the Bushmanland Plateau (Adams et al., 2004). These are results of numerous geomorphic cycles in the region (Partridge and Maud, 1987). The coastal lowlands are covered by recent sands and underlain by the crystalline basement rocks (Adams et al., 2004). The exposed domes, weathered materials which are extending to depths of 54-60m, fractured rocks as well as alluvium filled valleys characterises the escarpment zone of Namaqualand.

### **1.6.3 Climate**

Namaqualand has an arid to semi-arid climate with sparsely vegetated landscapes, dominated mainly by grass, shrubs as well as some occasionally succulents (Hohne and Hansen, 2008). Namaqualand falls in the tropical desert arid, hot climatic region of South Africa, according to the Koeppen classification (Adams et al., 2004). The climatic parameters are discussed below:

#### *1.6.3.1 Temperature*

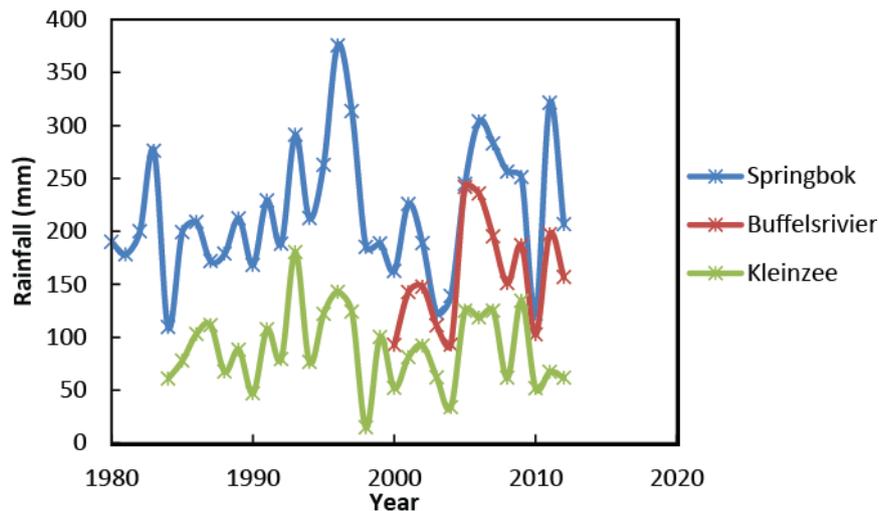
Temperatures in the region are characterised by large variations between maximum and minimum, daily and seasonal temperatures. The temperature ranges from a minimum of 2 degrees Celsius in winter to a maximum 45 degrees Celsius in summer (South African Weather Bureau, 2013).

#### *1.6.3.2 Rainfall*

West Namaqualand toward the coast receives winter rainfall while eastern Namaqualand receives rainfall during summer (Adams et al., 2004). In the west, the seasonal precipitation dominated by frontal systems from the Atlantic Ocean (Benito et al., 2010). The mean annual precipitation (MAP) in the region varies from 34 mm in the coastal zone area of Kleinsee to 321 mm at Springbok, for the period January 2000 to December 2012 (SAWB, 2013). The MAP increases from the west (coastal lowlands) to the east (escarpment zone) (Adams et al., 2004). Therefore, high lying (mountainous) regions receive more rainfall as compared to the lower lying areas and coastal plains. High rainfall in the mountainous areas is a result of orographic effects (Benito et al, 2011). Central Namaqualand is a winter rainfall area and precipitation occurs in the months of May to September. On the coastal region, precipitation in the form of fog is common and this contributes significant moisture to the coastal areas of Namaqualand (Olivier and van Heerden, 1999). Based on the catchment delineation made by Midgeley et al., (1994), the field area is in the F30 catchment. Decadal rainfall data for the Buffelsrivier, Kleinsee and Springbok showing average rainfall are shown in figure 1.6 (SAWB, 2013).

#### *1.6.3.3 Evapotranspiration*

Evaporation is high in Namaqualand, due to the arid climate of the region. Potential annual evapotranspiration is higher than the mean annual precipitation, in the range of 12-22 times more (Adams et al., 2004). The high evaporation rates have negative impacts on the environment, and results in the formation of evaporitic salts at the surface and on the subsurface. For the river deposits (alluviums), evaporations have been observed at depths of 91cm in the subsurface (Campbell et al., 1992). Evapotranspiration is high in densely vegetated areas with shallow water levels as compared to areas of sparse vegetation and deep water levels (Van der Sommen and Geirnaert, 1988). The potential evaporation in Namaqualand reportedly increases from west to east (Adams et al., 2004). High evaporation rates are observed during summer months as compared to winter months, and this is attributed to the high summer temperatures.



**Figure 1.6: Decadal annual precipitation records for Kleinzee, Buffelsrivier and Springbok from the South African Weather Bureau, 2013.**

#### 1.6.6.4 Vegetation

The Nama Karoo biome which comprises of the mixture of grasses and low shrubs characterises the vegetation in Namaqualand (Adams et al., 2004). The shrubs are classified as drought deciduous and have deep root systems (Adams et al., 2004). Annual mass flowering after sufficient rainfall is distinctive of Namaqualand. Vegetation is dependent on the groundwater availability, and are dominant in alluvial plains and riparian zones. The riparian shrubs and trees of the *acacia Karoo* are found in the alluvial aquifers of the Buffels River (Adams et al., 2004).

#### 1.6.4 Land Use Patterns

Indigenous Namaqualand people survived as hunters and gatherers for thousands of years back, and only around 2000 years ago was hunting and gathering overtaken by livestock herding mainly sheep and goats due to the area aridity (Webley 2007). The arrival of European farmers in the 1800s resulted in the land clearing and ploughing plant grain plants (Jowell and Folb, 2004). These have indicated a great impact on the Namaqualand ecosystem. The discovery of the mineral wealth of the area, with the mining and prospecting activities also had a great impact on the ecosystem. This started with the discovery of high grade copper in Springbok in 1850s by the European explorers (Carrick and Kruger, 2007). As the copper mining era was drawing to the close, there was a discovery of diamonds in the marine terraces of Oubeep close to Port Nolloth in 1925 (Carstens, 2001). The Buffels River catchment has active small scale mining activities of copper and diamond. Farming with sheep and goats as well as small scale irrigation farms are also found prevailing in the region.

### **1.6.5 Regional Hydrogeological Framework**

The prevailing scarcity of water resources in Namaqualand and the higher demands than the estimated available aquifers yields, result in needs to import water from other catchments (Pietersen et al., 2009). Water is transferred from the Orange River, having the transfers limited to major towns and mining areas only. The rural communities in the region depend on groundwater resources. The rivers, aquifers and water quality in the region are described below:

#### *1.6.5.1 Rivers in Namaqualand*

Rivers in Namaqualand are all ephemeral due to low rainfall in the region, with Orange River to the north of Namaqualand being the only perennial river. These rivers only flow after sufficient rainfalls (Adams et al., 2004). Regardless of the low annual runoffs in arid regions, peak rainfalls still cause peak flood discharge (Tooth, 2000). The main ephemeral rivers in the area are the Buffels River, Groen River and Swartlyntjies River (Adams et al., 2004). The largest of them in size is the Buffels River with a length of approximately 250 km. the Buffels River has its origin in the Kamies Mountains (1317m amsl) and discharges in the Atlantic Ocean at Kleinsee.

The Buffels River catchment is fed by the western part of the Bushmanland Plateau at an elevation of 900m. There are large variations on the drainage characteristics, channel widths, depth, sediment thickness, drainage density and the river terraces development of the Buffels River catchment (Adams et al., 2004). Soil cover exists in the tributaries, and this act as the major pathway of direct groundwater recharge. The thickness of the alluvial aquifers of the Buffels River increases in the lower lying areas as a result of change in topography and due to a decrease in sediment transportation, in contrast, there is a decrease in aquifer volume downstream and this is due to high evaporation rates and infiltration into alluvium losses (Adams et al., 2004). A geophysical profile reveals that for the Buffels River, water flow along the base of the alluvial aquifers and is stored in channel banks during dry months (Adams et al., 2004).

#### *1.6.5.2 Aquifers in Namaqualand*

Namaqualand is located in the arid to semi-arid western part of South Africa, and low rainfalls have a great impact on the net recharge of the local aquifers. Groundwater occurs in three different aquifer systems in the Namaqualand area. These are fractured bedrocks, weathered zones (megaliths) and the sandy alluvial aquifers. The fractured bedrocks and weathered zones form the basement aquifers of the region. The aquifers are reportedly closely interlinked (Adams et al., 2004). The aquifer's geometries are largely controlled by the underlying geology of the igneous and metamorphic rocks (mainly granites and gneisses), geomorphic developments as well as on its deformation history and structural evolution (Pietersen et al., 2009). These groundwater samples are fractionated by evaporation prior to infiltration (Leshomo, 2011). Recharge in areas with no direct infiltration are from regional flow from the neighbouring catchments.

#### (a) Basement Aquifers

The basement aquifers in Namaqualand comprise of the fractured bedrock aquifers and weathered regolith aquifers. These are linear systems that are associated with structurally controlled valleys, controlled by faults (Pietersen et al., 2009). In Namaqualand, the basement aquifers are prominent in the mountainous escarpment zone. The two aquifers are hydraulically interlinked, with weathered aquifers acting as reservoirs that recharge fractured bedrock aquifers (Adams et al., 2004). On contrary, in areas with extensive clays between the two aquifers the clay acts as a hydraulic barrier, shielding the aquifer linkage (Adams et al., 2004).

#### (b) Shallow Alluvial Aquifers

In Namaqualand, alluvial aquifers are associated with ephemeral rivers, paleo-channels and coastal plains. The aquifers associated with ephemeral river systems are reportedly shallower than those associated with the coastal plain (Pietersen et al., 2009). There are numerous minor alluvial aquifers for the Buffels River Catchment, due to the discontinuity of the alluvial fill along the river (Benito et al., 2011). These aquifers are disconnected by basement rock outcrops, which form natural barriers to the groundwater flow and result in small aquifers (Benito et al., 2011). The aquifers are reported to be significantly small in the upper and middle parts of the river catchment as compared to the lower catchment (Adams et al., 2004). The Spektakel and Kleinzee alluvial aquifers, situated in the lower catchment area are of significant sizes. The Spektakel aquifer is situated at Buffelsrivier communal area, where the river emerges from the escarpment on the inland edge of the coastal plain (Benito et al., 2011). The Kleinzee aquifer is at the river mouth before the Buffels River enters the Atlantic Ocean. Variations in water compositions within the aquifers were reported, depending on the aquifer depths, sand grain sizes, additional of fresh water by subsurface feeders, evapotranspiration effects and water level elevations (Benito et al., 2011).

#### *1.6.5.3 Groundwater Quality of Namaqualand*

Groundwater in Namaqualand is broadly characterised as relatively saline (Pietersen et al. 2009). High salinity contents are recorded in the lower lying regions, while higher lying regions in the region records lower groundwater salinity. High groundwater salinity contents are further recorded after flood events and during the dry summer months (Benito et al., 2010). Both shallow and deep aquifers in the region have saline groundwater (Adams et al., 2004). The source or sources of salinity to the groundwater in the region is still debatable. The high salt-loads in the region are reportedly of natural origin (Adams et al., 2004). These are caused by the dominant Na-Cl rainfall chemistry and by the preferential dissolution and leaching of the more evaporitic salts during infiltration (Adams et al., 2004). The concentrations of salts in precipitation are lower than in groundwater, having the high salts in groundwater concentrated by evaporation due to the arid nature of the area (Titus et al., 2002). Leshomo (2011) attributed the high salts concentrations to be derived from aquifer lithologies and from concentrations by evaporation. In addition to these predicted salinity sources, there are other

possible sources of salinity in the region. The salts can be of marine origin, brought about by the close proximity to the western coast. The mining activities in the region can also contribute to the elevated salts contents.

### **1.7. Scope and Outline of Thesis**

The main aim of this study is to determine sources and mechanisms of saline groundwater prevailing in the alluvial aquifers along the Buffels River, South Africa. The main body of the dissertation is a compilation of two stand-alone journal articles, each covering different aspects of saline groundwater assessment. The first article concentrates on the interpretation of major ions in groundwater. It further extend to determining the sources and mechanisms of groundwater salinity using  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{36}\text{Cl}/\text{Cl}$ ,  $^3\text{H}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  as well as the major ion rations. The second article concentrates on determining the recharge rate and mechanism to the alluvial aquifers using the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  stable isotopes and the chloride mass balance method. Some data (i.e. stable isotopes, field parameters and major ions) for the same area is used in the two articles for this thesis.

The preceding chapter gives the general background information to the study area and overview of the known Groundwater salinisation and recharge mechanisms. Chapter 2 and 3 are the journal articles. The last chapter is the general conclusion and recommendations drawn from the study, incorporating the two journal articles.

## Chapter 2: Salt sources to the shallow alluvial aquifers

NOTE: This material to be developed into a manuscript as follows:

Nakwafila, A.N., Miller, J.A., and Clarke, C.E., Salinisation processes in groundwater of the shallow alluvial aquifers lining the Buffels River, Northern Cape, South Africa. Target Journal: Journal of Arid Environments.

### Abstract

Salinisation of groundwater is a serious problem in large parts of Southern Africa. In the Buffels River of the Northern Cape Province in South Africa, salinisation of the shallow alluvial aquifers along the river is pronounced. This has resulted in the limitation of groundwater uses both for domestic, agricultural and commercial purposes. The region has an arid to semi-arid climate, with a mean annual rainfall of 175mm. The economy is dominated by small to medium scale mining activities, principally alluvial diamonds and Cu ores as well as small scale farming. In this study, the combined assessment of isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{36}\text{Cl}/\text{Cl}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and the major ion compositions and ratios were used in identifying the source(s) of salinity. The water character is predominantly Na-Cl. Salt loads vary between 181.40 and 9731.00 mg/L for  $\text{Na}^+$  and 298 and 14558 mg/L for Cl. The results indicate that there are multiple sources of salinity to the alluvial aquifers indicated by the lack of linear correlation between  $\delta^{18}\text{O}$  and electrical conductivity ( $r^2=0.0163$ ). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  stable isotopes indicate evaporation of groundwater prior or during infiltration. The concentration of dissolved ions by evaporation causes the salinisation of the groundwater. Furthermore, groundwater has high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, in the same ranges as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Spektakel Suite rocks. This indicates water-rock interactions, and the salts are from the dissolution of rock mass. Collectively the data indicate that although the region is arid to semi-arid the high salinity is not entirely derived from evaporation or recent wind-blown salts, but older salts hosted in alluvial gravels and sands are also a contributing factor.

Keywords: Salinisation, Chlorine-36, Groundwater, Semi-arid, Namaqualand, Ionic ratio

## 2.1 Introduction

Water supplies worldwide are beginning to deteriorate in quality because of increases in salt loads (Cartwright et al., 2004). The maximum permissible salt loads in drinking water are normally governed by both local regulations as well as international guidelines (WHO, 2006). Although many people think of salt loads in terms of Na-Cl only, salts exist in a number of other dissolved species such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Typically, water with elevated Na-Cl concentrations will have elevated concentrations of other species (Marie and Vengosh, 2001). Increased salt loads across the world have been driven by a wide variety of factors such as ancient seawater incursions and marine aerosols, leakage from fluid inclusions, evaporation and evapotranspiration of marine-influenced fluids, dissolution of evaporite deposits as well as prolonged water-rock reactions with Cl-bearing minerals (Leybourne and Goodfellow, 2007). Therefore, the types of salinisation and salinisation sources differ with different types of environments.

In arid and semi-arid environments, which typically suffer from water scarcity issues, groundwater salinisation is a prevailing problem. This is often driven by high evaporation rates, poor water management practices and the presence of palaeo-salt deposits (Gaye, 2001). Understanding the potential salt sources as well as the mechanisms by which the salts are transferred into the water system is therefore critical for the protection of water resources. Determining the origin of salinity is difficult for unconfined alluvial aquifers of the ephemeral rivers, which are often dominant in arid and semi-arid regions (Fabryka-Martin et al., 1991), because of the multiple salt sources to these aquifers (Gaye, 2001). Thus, saline water in these aquifers may have a unique source or a combination of sources (Nordstrom et al., 1989). The detection of the salinity sources to the alluvial aquifers is critical for sustainable water resources management, and groundwater quality purposes (Marie and Vengosh, 2001).

In South Africa, high salt contents are impacting the groundwater resources' quality across much of Namaqualand (Titus et al., 2000, 2002; Adams et al., 2004; Fersch, 2007; Benito et al., 2010 and Leshomo, 2011). However, there has been a broad divergence of opinions regarding the source(s) of these salts. The rainwater in the region has a Na-Cl character, and groundwater salinity is attributed to the dominant Na-Cl rainwater chemistry (Adams et al., 2004). Moreover, Namaqualand has high evaporation rates in comparison to the precipitation rates (Adams et al., 2004). The high salt concentrations in groundwater are said to be concentrated by evaporation (Benito et al., 2010). The high evaporation rates also result in the formation of evaporitic salts on the soil surfaces as well as on the unsaturated zone. The preferential dissolution and leaching of these salts by infiltrating groundwater also causes the salinisation of groundwater (Titus et al., 2002). The deep crystalline aquifers in Namaqualand are more saline (brines) than the shallow alluvial aquifers (Adams et al., 2004). Base-flow from the saline deep aquifers into the shallow aquifers also causes groundwater salinity (Leshomo, 2011). The dominant Na and Cl ions in the groundwater in Namaqualand, north of Aggeneys are reported to be derived from the aquifer lithology (Leshomo, 2011).

The alluvial aquifers of the Buffels River catchment also show elevated salinity levels. Both aquifers in the upper catchment (near the town of Rooifontein) and in the lower catchment (Spektakel Aquifer at Buffelsrivier) (Fig. 2.1) recorded high salinity concentrations (Benito et al., 2011). These aquifers are an important water source for domestic uses to the local communities as well as for mining activities in the area. State and privately owned farms in the region also depend on these aquifers. The source(s) of the elevated salinity levels to the alluvial aquifers along the Buffels River have not been determined. In addition to the above mentioned sources of salinity to groundwater in Namaqualand, there are other possible sources of salinity to the alluvial aquifers along the Buffels River. These include sea water intrusion as the river flows into the Atlantic Ocean, dry chloride fallouts as marine aerosols in coastal areas and salts from anthropogenic activities (i.e. the dominant mining activities in the region). Therefore, the objective of this research was to determine the source(s) of salinity and detect the possible control mechanisms to the salinisation of the groundwater in the alluvial aquifers lining the Buffels River. The combined assessment of isotopic ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{36}\text{Cl}/\text{Cl}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and the major ion compositions and ratios were used in identifying the source(s) of salinity to the alluvial aquifers. In addition, tritium ( $^3\text{H}$ ) was used to determine the groundwater age of the groundwater.

## 2.2 Study Area

The study was done on the alluvial aquifers lining the Buffels River of Central Namaqualand in the Northern Cape Province, South Africa (Fig. 2.2). There are no perennial rivers in the province, with the Orange River to the north at the South African-Namibian border being the only exception. People depend on groundwater except the ones that live in major and mining towns that are supplied with piped water from the Orange River. The Buffels River catchment, at an area of 9250 km<sup>2</sup> (Fig. 2.1) is the largest ephemeral river in Namaqualand, and contains numerous alluvial aquifers, which are the primary source of water to the communal communities in the region (Benito et al., 2011).

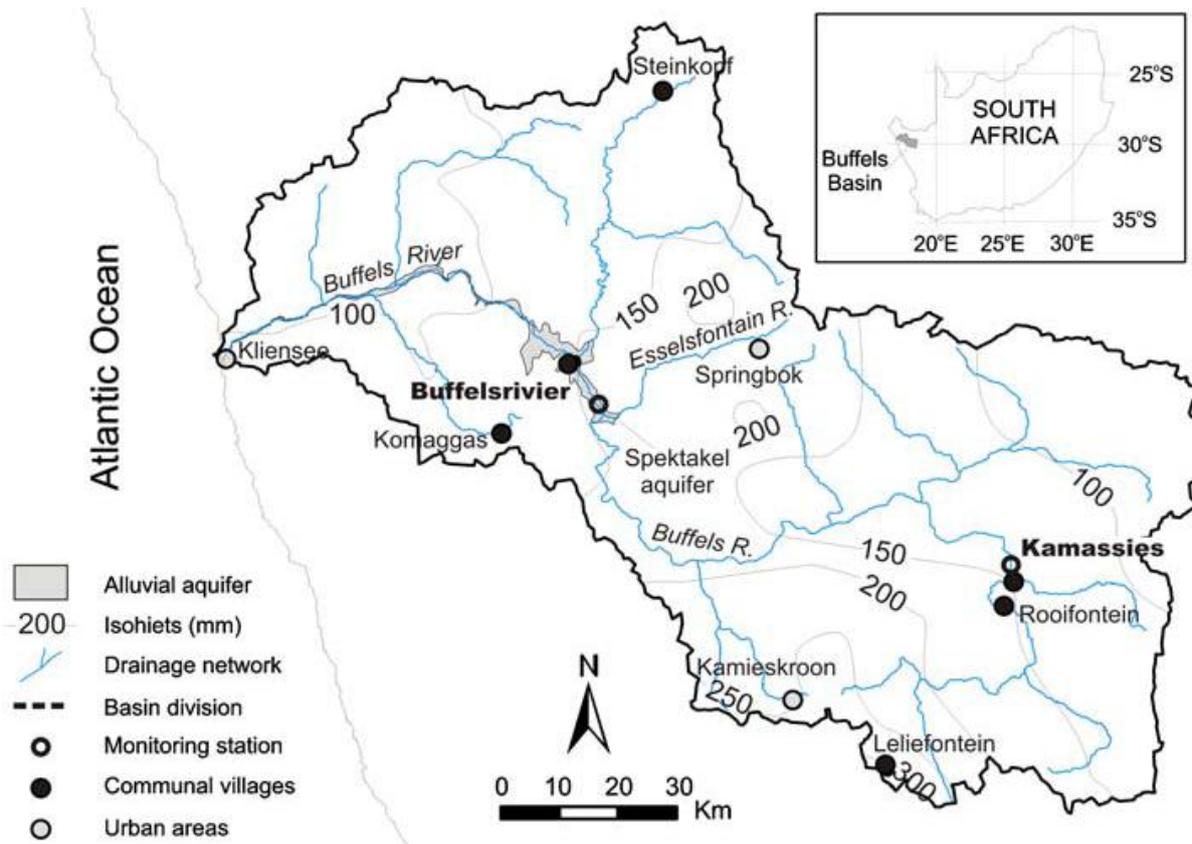


Figure 2.1: The Buffels River drainage basin, indicating the extent of the shallow alluvial aquifers. Taken from Benito et al., 2010.

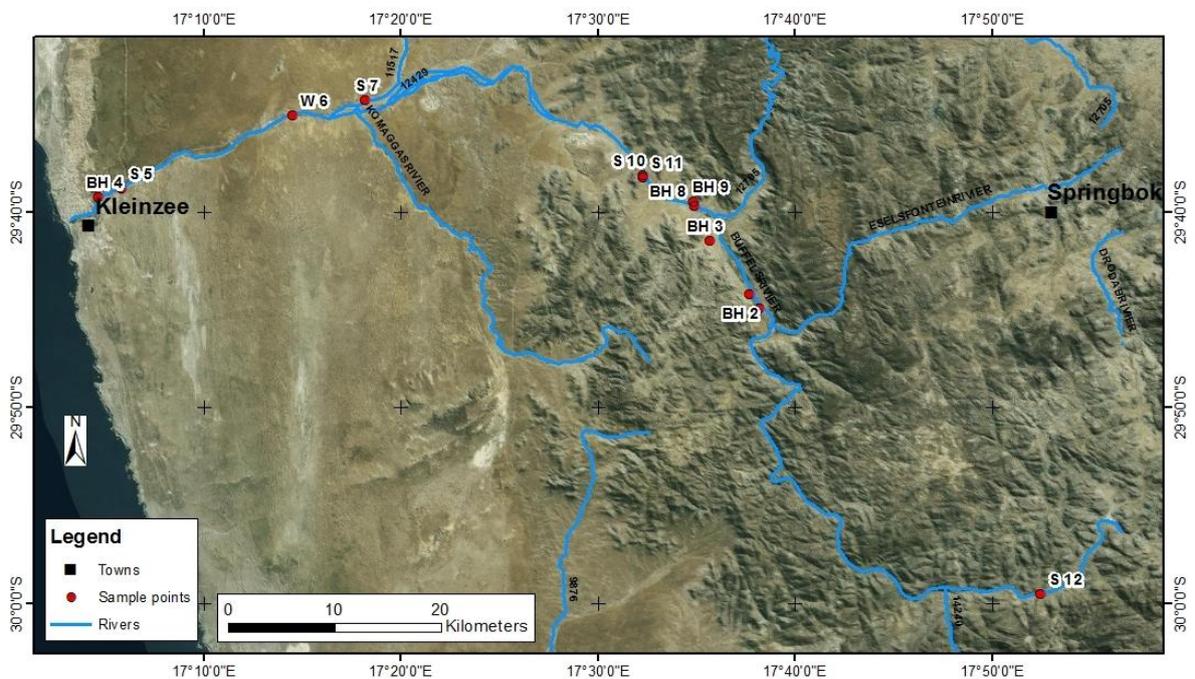


Figure 2.2: Distribution of the sampled groundwater locations from the N7 National road to Kleinzee.

### **2.2.1 Geological Environment and Hydrogeological Setting**

The Buffels River drains through the Paleoproterozoic to Neoproterozoic Namaqualand Metamorphic Province (NMP) of the Namaqua-Natal Belt. The NMP is subdivided into four subprovinces namely the Richtersveld, Bushmanland, Gordonia and Kheis Subprovinces (Blignault et al., 1983; Hartnady et al., 1985). The Buffels River catchment flows through the Mesoproterozoic Bushmanland Subprovince, which is the largest of the four subprovinces of the NMP (Blignault et al., 1983). The Bushmanland Subprovince comprises of deformed orthogneisses and granitic intrusions, which are biotite-bearing (Waters, 1990). The dominant rock units within the Bushmanland Subprovince are two Mesoproterozoic granitic intrusive suites of the Little Namaqualand Suite and the Spektakel Suite, which show intrusive relationships with the Gladkop Suite granites. These granitic suites intruded into sediments which are now represented by supracrustal gneisses of the Kamiesberg and Bushmanland Groups (Moore, 1989). These rocks are metamorphosed to medium-high grades attaining an amphibolite and granulite metamorphic facies (Jacobs et al., 1993). The Buffels River catchment bedrock comprises of impermeable meta-sedimentary rocks, basic granites and ultrabasic intrusive rocks (Marais et al, 2001). The detailed geology context is given in Chapter 1.

There are no surface waters in the region; except for the Orange River which forms a national boundary between Namibia and South Africa. The alluvial aquifers lining the ephemeral rivers are therefore sole water sources in the region adding to the deep crystalline aquifers and to the piped water from the Orange River to big towns like Springbok and Kleinsee (Adams et al., 2004). The Buffels River catchment (Fig. 2.1) contains numerous minor alluvial aquifers, which are results of the alluvial fill discontinuities along the river (Benito et al., 2011). The basement rocks outcrop on the Buffels River, forming natural barriers to the groundwater and further resulting in small aquifers. The aquifers are significantly small in the upper and middle parts of the river catchment as compared to the lower catchment (Adams et al., 2004). The Spektakel and Kleinsee alluvial aquifers, situated in the lower catchment are the only aquifers of significant sizes in the catchment. The Spektakel aquifer is situated at the Buffelsrivier communal area, where the river emerges from the escarpment on the inland edge of the coastal plain (Benito et al., 2011). The Kleinsee aquifer is at the river mouth before the Buffels River enters the Atlantic Ocean. Variations in water compositions within these aquifers were reported, and have been attributed to differences in the aquifer depths, sand grain sizes, addition of fresh water, evapotranspiration effects and water level elevations (Benito et al., 2011).

### **2.2.2 Climate and Geomorphology**

Namaqualand is characterised by three geomorphologic regions namely: the coastal lowland, an escarpment zone and the Bushmanland Plateau (Adams et al., 2004). The topography varies from a low relief and altitude coastal zone to a high altitude escarpment zone. The coastal lowlands are covered by recent sands, and overlain by the crystalline basement rocks (Partridge and Maud, 1987). The escarpment is characterised by weathered materials, fractured rocks and alluvium filled valleys.

The region has an arid to semi-arid climate. The winter rainfalls are prevailing in the western Namaqualand, and they caused by frontal systems from the Atlantic Ocean. The frontal systems give rise to gentle rainfalls and drizzles (Benito et al., 2011). The precipitation amounts are high in the mountainous areas, with an average annual precipitation of 450mm at the Kamies Mountains headwaters and decreases towards the coast, with an annual precipitation of 110mm at Komaggas on the coastal plain (Benito et al., 2011). The high rainfalls in mountainous areas are due to the orographic effects. Temperature in the region is variable, having maximum temperatures of 45 degrees Celsius in summer and minimums sub-zero temperatures in winter (SAWB, 2013). The evaporation rates in the region are high as a result of arid climate conditions. The potential annual evapotranspiration in the region is 12-22 times more than the mean annual precipitation (Adams et al., 2004).

### **2.2.3 Mining**

Mining in Namaqualand started with the discovery of copper in Springbok in the 1850s by the European explorers (Carrick and Kruger, 2006). Other numerous deposits were also found, resulting in enormous heavy metals mining activities in the area. As the copper mining era was drawing to the close, diamonds were discovered in the marine terraces of Oubeep close to Port Nolloth in 1925 (Carstens, 2001). This resulted in massive diamond mining and prospecting a few kilometers from the coast and along rivers. The mining activities have a great impact on the ecosystem, including on the groundwater resources of the area. Most of this mining activities use groundwater for their mining operations (Marais, 1981). Having the shallow groundwater level in the area, the mining activities also disturbs the groundwater levels. The percolations of wastewater from the mining activities to the groundwater can also contaminate the groundwater; especially in the shallow unconfined aquifers. In the study area, there are no mining activities in the upper Buffels River catchment. All the mining activities are in the lower catchment, with the Spektakel Mine at Buffelsrivier the upstream mine and numerous diamond mining activities along the river towards the coast.

## **2.3 Materials and Methods**

### **2.3.1 Field Sampling**

A total of 31 groundwater samples were taken from six boreholes and three hand-dug wells along the Buffels River. In places where boreholes were absent; a hand auger was used to access the shallow groundwater. The samples were taken from existing boreholes mainly used for domestic, livestock and irrigation purposes. A monitoring borehole at the Spektakel Mine was also sampled. All the sampling locations are shallow (the deepest is at 7 m) and hence all the water samples are interpreted to be from the same shallow alluvial aquifer system. Groundwater samples were collected in three seasons, this being in early March 2013 before the wet season, in September 2013 after the wet season and in February 2014 again before the wet season. This was to observe temporal variations of geochemical and isotopic parameters. Not all sampling sites could be sampled each

time. Heavy rain during the winter of 2013 washed out two of the hand dug wells that were sampled during the summer of 2013. However, these hand dug wells had been reinstated by the third sampling round in the summer of 2014. Groundwater could also not be accessed by the augur during the dry season (February 2014).

The boreholes were pumped until the groundwater measurements of the EC and pH were stable before sampling. For the hand augured sites and hand dug wells, samples were taken directly using a bailer and no pre-sampling pumping was done on these sites. Groundwater samples were taken at each site for the analysis of anions, cations and environmental isotopes ( $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{87}\text{Sr}$  and tritium). The cations, anions and stable isotopes samples were taken for all the sampling seasons, depending on the accessibility (Table 2.1). The  $^{36}\text{Cl}$  samples were taken for two seasons (September 2013 and February 2014), while  $^{87}\text{Sr}$  and tritium samples were only taken in February 2014.

The cations and anions samples were filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter and collected in clean 50ml conical Polypropylene (PP) tubes, having the tubes flushed first with sampled water. The cation samples were acidified with nitric acid ( $\text{HNO}_3$ ), to prevent the metals from precipitating out. The stable isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) samples were also filtered and collected in clean 15ml conical PP tubes.  $^{36}\text{Cl}$  and  $^{87}\text{Sr}$  isotope samples were collected in clean 0.5L polyethylene (PE) bottles, while  $^3\text{H}$  was collected in a 1litre PE bottle. These were kept cold in a cooler box with ice in the field and refrigerated after the field until they were analysed.

Table 2-1: Summary of sampling collection for the groundwater

Sample No	March 2013	September 2013	February 2014
<b>Boreholes</b>			
BR13-1B01	X	X	X
BR13-1B02	X	X	X
BR13-1B03	X	X	X
BR13-1B04	X	X	X
BR13-1B08	X	X	X
BR13-1B09	X	X	X
<b>Hand Dug Wells</b>			
BR13-1W06	X	X	
BR13-1W10	X		X
BR13-1W11	X		
<b>Field Augured Wells</b>			
BR13-1S05	X	X	X
BR13-1S07	X	X	
BR13-1S12	X	X	

At each sampling site, the field parameters pH, electrical conductivity, temperature and alkalinity were measured. The pH, electrical conductivity (EC), and temperature, were measured using the portable

EXTECH EC500 pH/Conductivity probe. The probe was calibrated daily, before taking any measurements, against the pH 4 and 7 standards and the EC 1413  $\mu\text{S}/\text{cm}$  standard to verify the calibrations. The temperature readings were taken first for every site, to avoid atmospheric alterations. Alkalinity was also measured in the field by titration against 1.600N sulphuric acid with the HACH digital titrator kit.

In addition to these samples, rainwater samples were collected from the Naries Namaqua Guesthouse approximately 20 km west of Springbok and from the police station at Kleinzee, as well as at Komaggas where the South African Meteorological Bureau has a monitoring station. Rainwater quantities are extremely variable and are collected whenever there is rain. This was collected at 8am in the morning by residents at these three stations. The people collecting the samples were asked to keep the samples cool until collection. The samples were analysed for Cl content and stable isotopes of oxygen ( $^{18}\text{O}$ ) and hydrogen ( $^2\text{H}$ ), because of the limited volume of materials used in collecting the samples. Once these had been analysed the remaining samples from each collection period were pooled for the  $^{36}\text{Cl}$  analyses. A total of 10 pooled rainwater samples were processed and sent to Australia for analysis. This was done to provide a bench mark on the  $^{36}\text{Cl}$  on precipitation, which is the input parameter to the groundwater system. The rainwater samples were pooled as the chloride concentration in the rainwater samples was very low and thus a larger volume of sample water was needed to raise the  $^{36}\text{Cl}$  concentration to a detectable level.

### **2.3.2 Geochemical Analysis**

The samples were sent to analytical laboratories for analysis, keeping the time between their collection and their analysis less than a month.

#### *2.3.2.1 Cations, Anions and Trace elements*

Major cations were analysed using a Thermo iCAP inductively coupled plasma optical emission spectrometry (ICP-OES) in the Central Analytical Facility (CAF) laboratory, at the Department of Earth Sciences, Stellenbosch University. Trace elements were determined by using an Agilent 7700 inductively coupled plasma mass spectrometry (ICP-MS) also at CAF laboratory. The instruments are calibrated on a daily basis using the National Institute of Standards and Technology (NIST)-traceable standards. For instrument stability, regular control standards are analysed throughout the run. The percentage errors for the cations analyses did not exceed 10%.

Anion analyses for the samples collected in 2013 were done on a DIONEX DX-129 ion chromatograph (IC) at the laboratory in the Department of Soil Sciences at Stellenbosch University. The anions have maximum detection limits, upon which they can be detected by the IC (Table 2.2). Anions of high concentrations above the detection limits were diluted based on the corresponding EC values. In this case, errors in dilution may have occurred resulting in inaccurate data. Anion samples collected in February 2014 were analysed using Waters 717 Autosample-conductivity detector-

Agilent 1120 pump ion chromatography at the CAF laboratory in the Department of Sciences, University of Stellenbosch. The samples were diluted to 10X and 100X, due to high salinity levels in the groundwater indicated by high EC readings measured in the field. The data was corrected using a polynomial fit to four calibrations Spectrascan SS-028555 standards plus a blank. The analytical errors also did not exceed 10%. Considerations of differences in analysing machines must be considered for data interpretations.

Table 2-2: Detection limits of the DIONEX DX-129 IC

Anion	Detection limit (mg/l)
Cl	6
NO <sub>3</sub>	30
PO <sub>4</sub>	30
SO <sub>4</sub>	30

### 2.3.2.2 Environmental Isotopes

#### (a) Stable Isotopes

Stable isotope samples (<sup>18</sup>O and <sup>2</sup>H) were sent to the Water Resources Centre, University of KwaZulu Natal. These were analysed using a Los Gatos Research (LGR) DT-100 Liquid Water Isotope Laser Analyser. A set of three standards was placed in the auto-sampler tray before every 5 samples to be analysed as well as after the last 5-sample set. The standards used have been prepared by calibration against the following known standards: LGR2 ( $\delta^2\text{H}$  -117.00,  $\delta^{18}\text{O}$  -15.55), VSMOW2 (IAEA) ( $\delta^2\text{H}$  0.0,  $\delta^{18}\text{O}$  0.0) and IA-RO53 (IAD) ( $\delta^2\text{H}$  -61.97,  $\delta^{18}\text{O}$  -10.18). Each sample and standard was sub-sampled and analysed 6 times. The standard deviation of the <sup>2</sup>H results was less than 1.5permil and for the <sup>18</sup>O samples, less than 0.3 permil (‰). The analyser gave the values as <sup>2</sup>H/H and <sup>18</sup>O/<sup>16</sup>O ratios. These ratios are then converted to  $\delta$  using the standard isotope equation:

$$\delta = \frac{R_A - R_{std}}{R_{std}} \times 1000$$

#### (b) <sup>36</sup>Cl Isotope

For the chlorine-36 analyses, the chloride concentrations of the samples were first determined, ensuring they have a concentration of 5 mg/L or more. 45ml of each groundwater sample was then acidified with concentrated nitric acid and added to a dilute solution of silver nitrate (AgNO<sub>3</sub>) in a dark room. Silver chloride (AgCl) precipitated out, and was left to dry overnight in an oven set at 60°C. The precipitate was placed in 50ml conical PP tubes, sealed and wrapped in a foil because AgCl is sensitive to light. This was sent to the laboratory at Australia National University in Canberra, Australia for the <sup>36</sup>Cl analysis. The samples were analysed using the accelerator mass spectrometry. The

chlorine concentrations were given as a ratio of  $^{36}\text{Cl}/\text{Cl}$ , with Cl representing  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  (the stable chloride isotopes) and  $^{36}\text{Cl}$  is the radioactive chloride isotope.

(c)  $^{87}\text{Sr}$  Isotope

The  $^{87}\text{Sr}$  analyses were performed on a Nu instruments NuPlasma HR MC-ICP-MS in the Department of Geological Sciences, at the University of Cape Town. The filtered groundwater samples, filtered in the field were used for the analysis. 6ml of each sample was dried down in a Teflon beaker. Subsequent to this the nitric acid ( $\text{HNO}_3$ ) was added and the sample was again dried down, having the process repeated twice. After the sample was dried down the second time, 1.5ml 2M  $\text{HNO}_3$  was added. The sample was then ready for Sr chemistry. The Sr chemistry involved putting the sample through a standard cation exchange column which extracted the Sr for analysis. Sr isotopes were analysed as 200ppb 0.2%  $\text{HNO}_3$  solution. A reference standard NIST SRM987 and an  $^{87}\text{Sr}/^{86}\text{Sr}$  normalizing value of 0.710255 were used. The Sr isotope data was corrected for Rb interference and instrumental mass fractionation using the exponential law and an  $^{86}\text{Sr}/^{88}\text{Sr}$  value of 0.1194.

(d) Tritium

Tritium concentrations were analysed at iThemba LABS at Witwatersrand University in Johannesburg. The 1000ml samples collected in the field were distilled into round glass container to collect 500 ml of the sample water after which 4g of sodium peroxide was added. The solution is then weighed and then introduced into an electrolytic cell made up of two concentric cells, one inside the other and which are insulated from each other. A direct current of 10-15 Ampere at 12Volts is passed through the cell which is cooled continuously due to heat generation within the cell. After several days the volume is reduced to 20ml, a reduction of 25 times. This reduction corresponds to a tritium enrichment of a factor of about 20. Standards of known tritium concentration are used to confirm the enrichment factor. The 20ml sample goes through a vacuum distillation using a gas flame to heat the sample. The sample is reduced to 10ml and added to 11ml of Ultima Gold LLT LSC cocktail in a counting vial. The final sample is placed into a Packard Tri-Carb 2770TR/SL which is a low level liquid scintillation analyser. The samples are counted for at least 3 cycles of 4 hours to improve analysis accuracy and to eliminate outliers. The results are expressed as tritium units (TU).

## 2.4 Results

### 2.4.1 Field Parameters

The measured physical parameters (field parameters) in the alluvial aquifers of the Buffels River for all the sampling seasons are given in Table 2.3. The groundwater samples have a temperature that ranges from 19.8-29.5°C, 12.8-23°C and 22.1-32°C respectively for the three sampling seasons. The pH values for all the three sampling seasons are mainly neutral, with an acidic groundwater sample with a pH of 4.8 measured at the hand dug well (W06) in March 2013. Low pH values of 5.1 and 5.4

were also measured at B09, the treated shaft water used at the Spektakel Mine in September 2013 and February 2014.

The sampled groundwater is relatively saline, with minimum EC values of 1.4mS/cm, 1.4mS/cm and 1.6mS/cm respectively for the three sampling seasons. These were measured at BH01, BH02 and S12 (Fig.2.2), and these are all situated before the mining activities along the river. The highest EC was recorded at the hand augured well S07 for all the sampling season, measuring EC values greater than 20mS/cm (the detection limit of the used EXTECH probe). Salt precipitates are visible in the surrounding of the well (Fig.2.3). Temporal variations exist between the EC values of the groundwater samples taken during the wet season and those taken during the dry seasons. High EC values were measured during the dry seasons of March 2013 and February 2014, as compared to those taken in the wet season of September 2013 (Fig.2.4). The EC values vary spatially too, having low EC values measured in the groundwater samples upstream, before the mining activities (S12, BH1, and BH2) but this is not consistent towards the coast. High EC values were measured at boreholes close to the mining activities (BH04, S07 and BH08).



*Figure 2.3: The salt precipitates on the soil surface at S07*

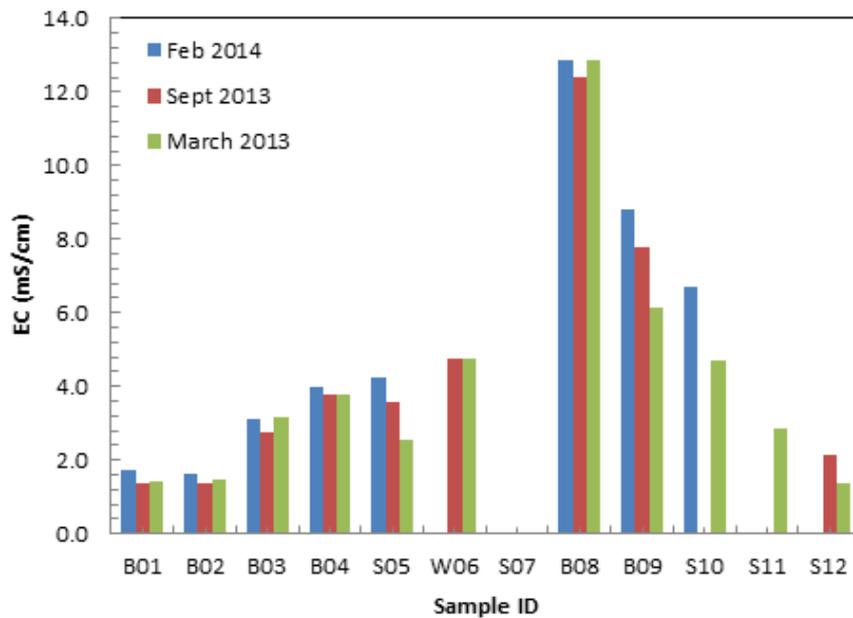


Figure 2.4: Electrical conductivity comparison for the three sampling campaigns

Table 2-3: Field parameters of the groundwater samples

	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
<b>Sample location</b>												
Latitude	29°44.927'	29°44.171'	29°41.481'	29°39.209'	29°38.777'	29°35.074'	29°34.286'	29°39.697'	29°39.469'	29°38.144'	29°38.233'	29°59.523'
Longitude	017°38.199'	017°37.686'	017°35.683'	017°04.651'	017°05.826'	017°14.492'	017°18.176'	017°34.887'	017°34.867'	017°32.281'	017°32.304'	017°52.473'
<b>Temp (°C)</b>												
Mar-2013	24.0	24.2	28.4	26.3	26.3	25.6	25.9	27.2	28.3	28.7	29.5	19.8
Sep-2013	22.4	22.4	20.4	18.2	16.6	22.2	21.5	22.9	23.0			12.8
Feb-2014	27.8	29.1	32.0	22.1	29.8		31.7	28.9	31.8	32.0		
<b>pH</b>												
Mar-2013	7.3	7.2	6.8	7.0	6.6	4.8	7.3	7.2	7.5	7.2	7.5	7.6
Sep-2013	7.3	7.4	6.9	7.3	7.0	7.3	7.6	7.4	5.1			7.5
Feb-2014	7.3	7.5	6.6	6.7	6.9		7.0	6.8	5.4	7.2		
<b>EC (mS/cm)</b>												
Mar-2013	1.4	1.5	3.2	3.8	2.6	4.8	20.0	12.9	6.1	4.7	2.9	1.4
Sep-2013	1.4	1.4	2.8	3.8	3.6	4.8	20.0	12.4	7.8			2.2
Feb-2014	1.7	1.6	3.1	4.0	4.2		20.0	12.8	8.8	6.7		
<b>Alkalinity (mg/L)</b>												
Mar-2013	87.6	536	116	164	84	56	228	310	120	128	118	528
Sep-2013	78	118	142	154	232	108	464	430	16			162
Feb-2014	120	80	140	216	190		296	416	2	114		
<b>B-Borehole</b>												
<b>S-Field augured shallow wells</b>												
<b>W-Hand dug wells</b>												

## 2.4.2 Cations and Anions

The major cations and anions for all the three sampling seasons are presented in Table 2.4. The trace elements results with their percentage errors are also given in Table 2.5. The trace elements are low in the groundwater samples from all the sampling seasons. The analytical results indicate the abundance of the anions in the following order  $Cl > SO_4 > HCO_3$ , with  $HCO_3$  greater than  $SO_4$  at B01, B02, and S12. Chloride is the dominant anion and its concentrations range from 298-14588 mg/L, 278-12748mg/L and 209-11217mg/L for the three sampling seasons. High Cl concentrations were

recorded in March 2013 (dry season) and these reduced during the wet season (September 2013) with further reduction in February 2014. The highest Cl concentrations were recorded at S07 for all the sampling seasons. The groundwater samples with high chloride also measured high EC (Fig. 2.5).

The cations are in the order of Na>Ca>Mg>K, with sodium (Na) being the dominant cation in all the sampling seasons. Sodium ranges from 143.2-4933 mg/L, 181.4-9731 mg/L and 134-13650 mg/L respectively for all the sampling seasons. The Na concentrations are high in February 2014 and low in March 2013, both in wet seasons. The groundwater samples with high Cl also have high Na, and Na/Cl have a strong positive correlation for all the sampling seasons (Fig. 2.6). Piper plots and stiff diagrams were plotted to determine the groundwater character of the alluvial aquifers (Fig. 2.7 and 2.8). The groundwater is Na-Cl in character for all the sampling seasons, with only two boreholes containing Na-HCO<sub>3</sub> water types in the samples taken in March 2013 and sample B09 of Na-SO<sub>4</sub> character in February 2014. The ionic ratios of several ions (i.e. Ca/Sr, Na/Cl, Mg/Cl) were used in determining the salinity source(s) to the groundwater. The Ca/Sr also shows a positive correlation (Fig. 2.9). Additionally, the major ions/Cl ratios are not linear, but indicate a positive correlation (Fig. 2.10).

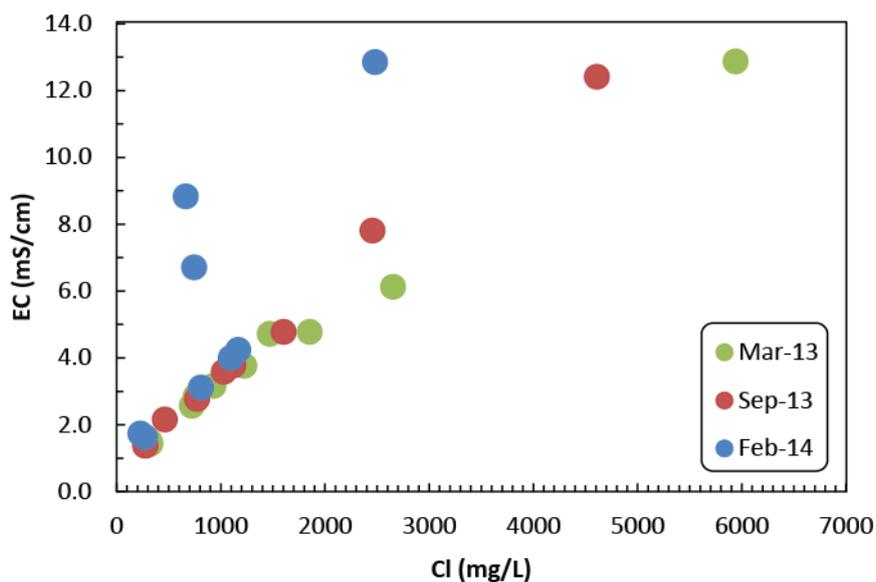


Figure 2.5: EC-chloride concentration relationship in the groundwater samples

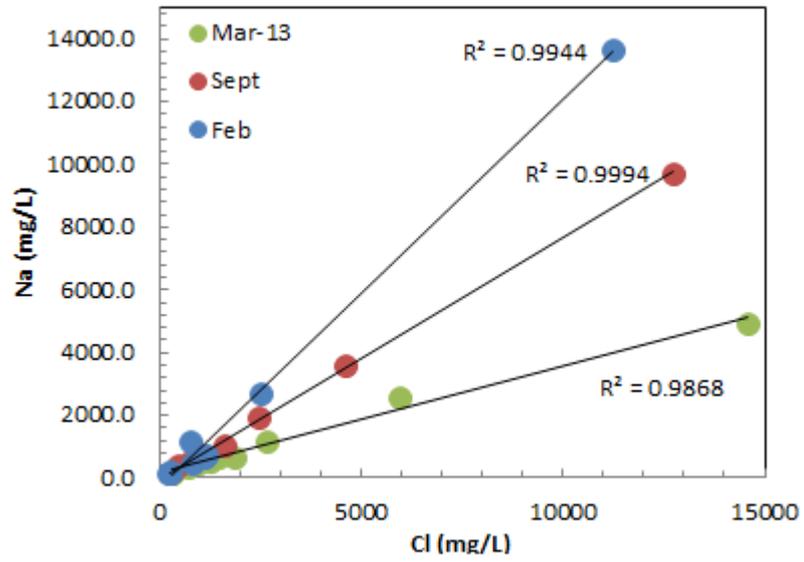


Figure 2.6: The Na-Cl relationship of the groundwater samples

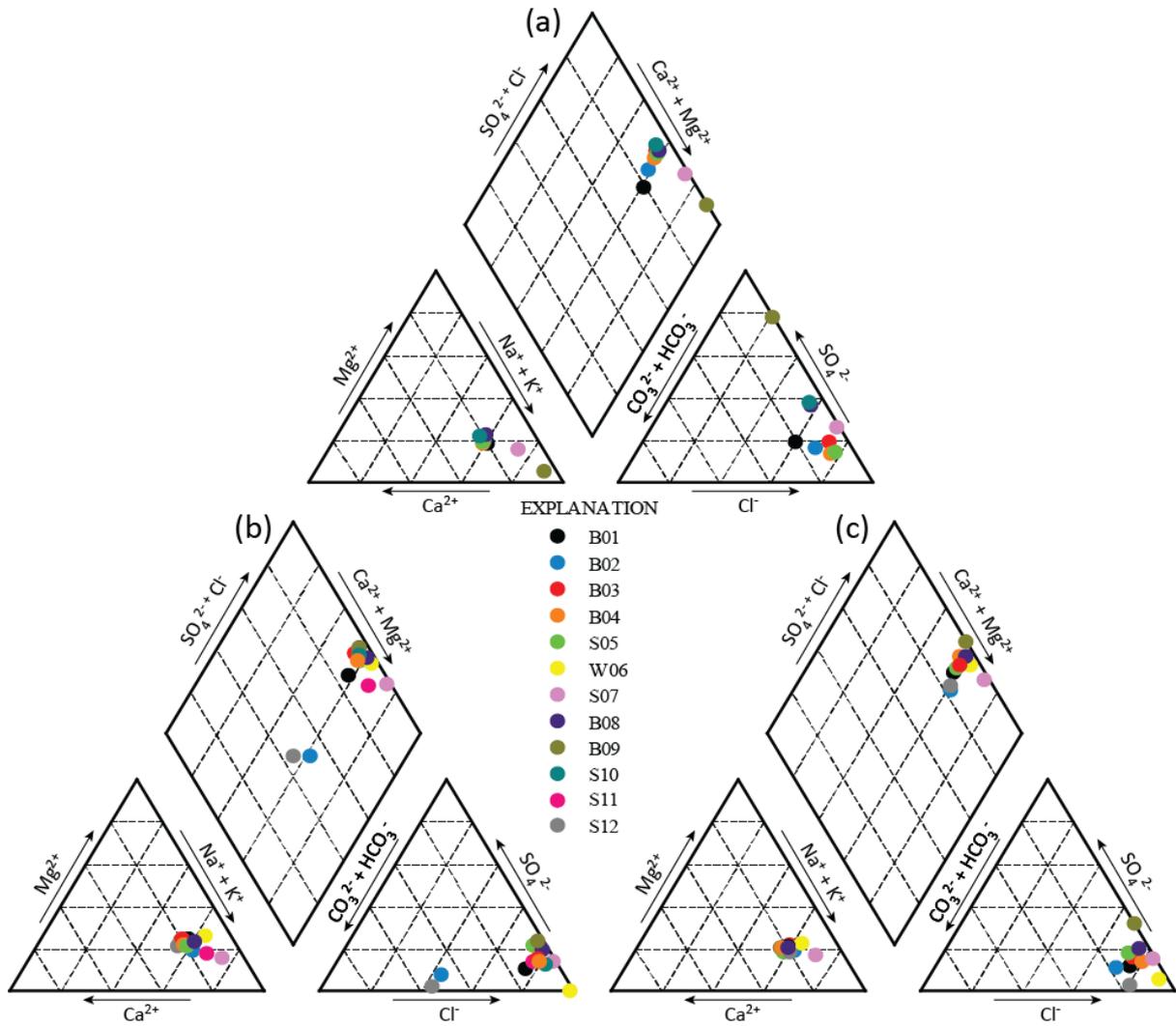


Figure 2.7: Piper plots of the groundwater samples taken (a) in February 2014, (b) March 2013 and (c) September 2013

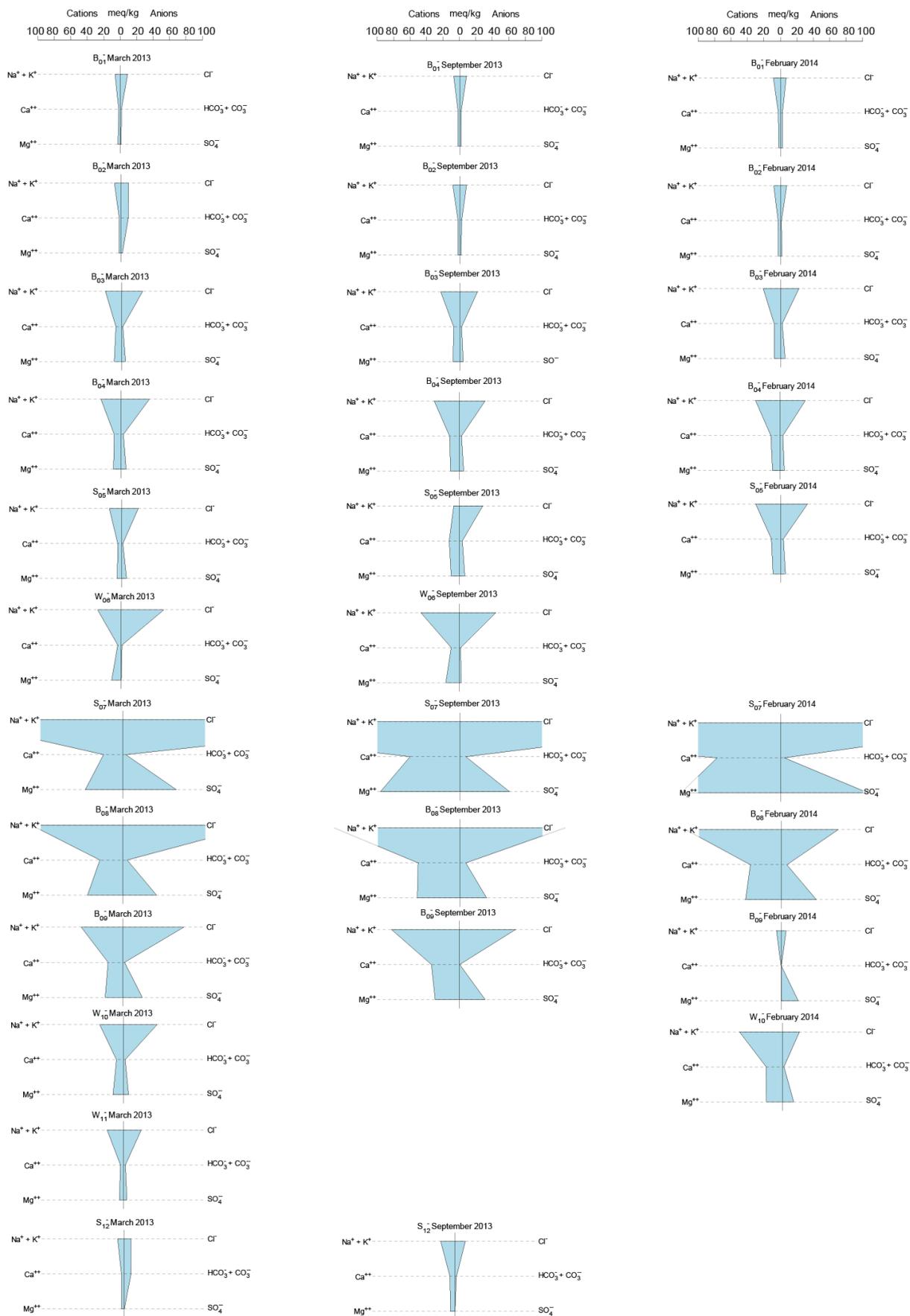


Figure 2.8: Stiff diagrams for the sampled groundwater

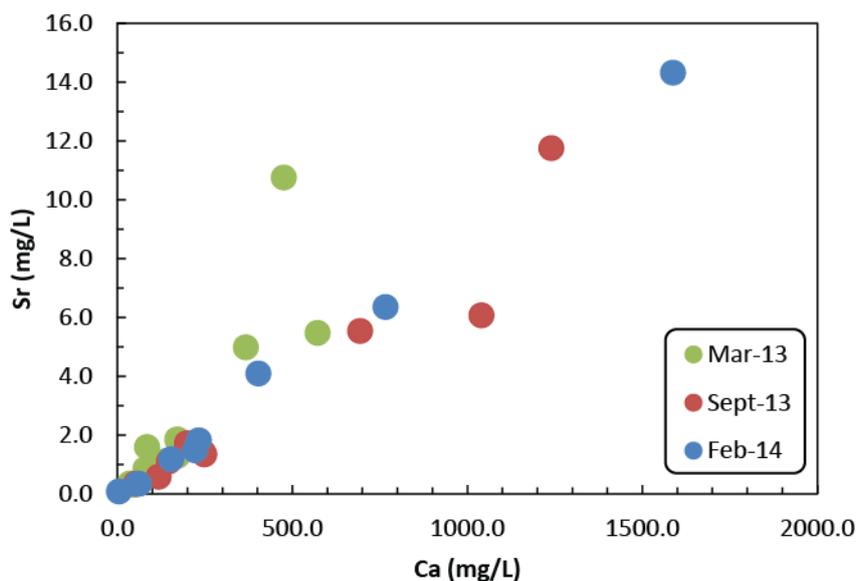


Figure 2.9: Ca/Sr relationships in the groundwater

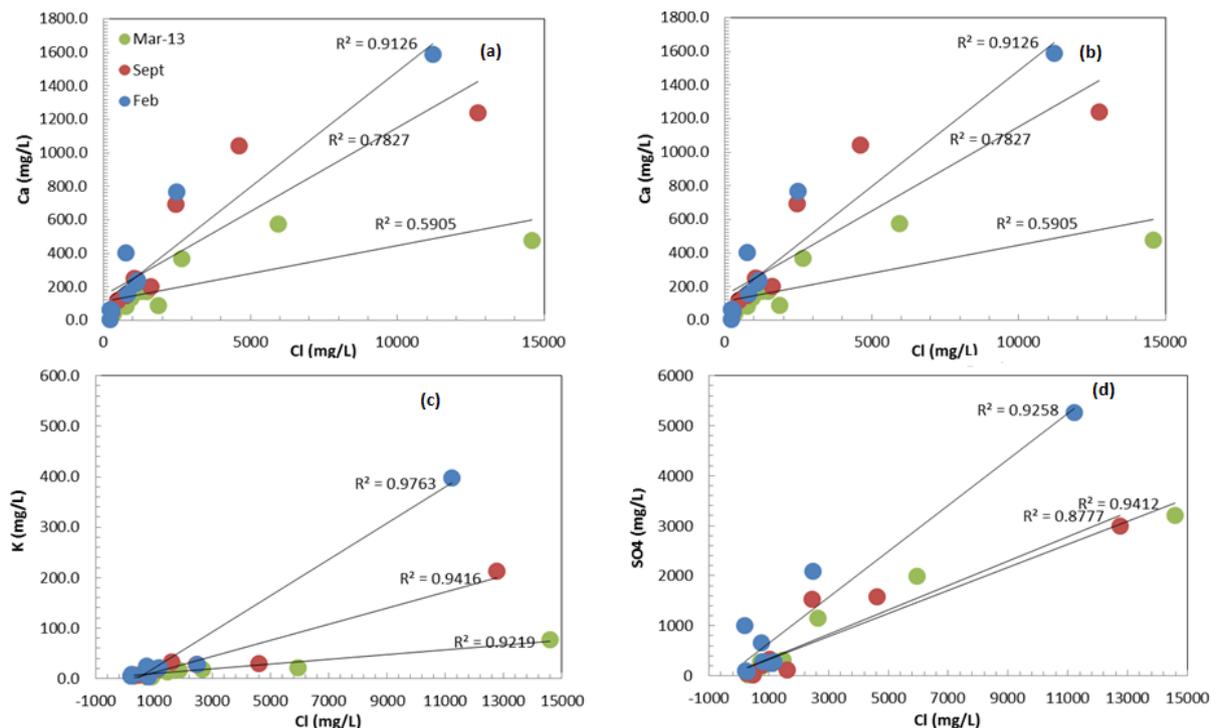


Figure 2.10: The correlation plots of chloride against (a) Calcium, (b) Magnesium, (c) Potassium and (d) Sulphate

Table 2-4: Cations and anions of the groundwater samples

	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
<b>Cl (mg/L)</b>												
Mar-2013	325.0	320.0	930.0	1229.0	725.0	1854.0	14588.0	5944.0	2657.0	1472.0	763.0	298.0
Sep-2013	278.0	281.0	774.0	1123.0	1030.0	1606.0	12748.0	4612.0	2459.0			466.0
Feb-2014	230.8	273.3	811.7	1097.5	1168.6		11216.7	2483.8	209.2	746.0		
<b>SO<sub>4</sub> (mg/L)</b>												
Mar-2013	58.0	71.0	245.0	286.0	284.0		3205.0	1990.0	1144.0	307.0	187.0	16.0
Sep-2013	54.0	56.0	211.0	255.0	331.0	111.0	2986.0	1580.0	1526.0			15.0
Feb-2014	96.1	86.4	282.3	254.8	274.6		5264.2	2086.4	1004.5	664.3		
<b>NO<sub>3</sub> (mg/L)</b>												
Mar-2013			31.0									
Sep-2013		28.0										
Feb-2014			36.2				114.5			73.1		
<b>HCO<sub>3</sub> (mg/L)</b>												
Mar-13	87.6	536.0	116.0	164.0	84.0	56.0	228.0	310.0	120.0	128.0	118.0	528.0
Sep-2013	78.0	118.0	142.0	154.0	232.0	108.0	464.0	430.0	16.0			162.0
Feb-2014	120.0	80.0	140.0	216.0	190.0		296.0	416.0	2.0	114.0		
<b>Ca(mg/L)</b>												
Mar-2013	36.7	46.6	134.4	173.2	99.0	86.0	476.6	573.5	367.6	171.7	80.7	
Sep-2013	53.5	54.5	148.5	244.7	249.0	199.3	1241.0	1041.0	695.0			118.4
Feb-2014	62.4	57.7	155.0	222.7	234.0		1589.0	767.2	6.0	403.8		
<b>Mg (mg/L)</b>												
Mar-2013	33.5	31.5	106.4	115.0	66.2	142.6	566.1	533.1	266.8	155.2	65.2	
Sep-2013	34.8	33.8	100.5	131.9	121.5	201.6	1203.0	643.7	365.0			62.8
Feb-2014	32.8	32.9	93.7	110.7	118.1		1513.0	538.3	3.6	239.8		
<b>Na (mg/L)</b>												
Mar-2013	143.2	185.6	446.9	562.8	341.0	655.6	4933.0	2606.0	1169.0	664.2	465.8	
Sep-2013	181.4	207.6	535.1	703.9	745.2	1074.0	9731.0	3566.0	1916.0			394.5
Feb-2014	208.5	184.5	485.4	674.1	702.7		13650.0	2699.0	134.4	1208.0		
<b>K (mg/L)</b>												
Mar-2013	4.6	7.0	3.2	17.1	17.4	16.9	77.1	21.3	18.3	12.8	10.4	
Sep-2013	5.8	6.5	3.0	18.5	18.8	32.1	212.7	29.8	28.2			
Feb-2014	7.8	7.0	3.3	19.7	22.0		397.0	27.6	4.2	25.2		

Table 2-5: Trace elements measured on the groundwater samples taken from the alluvial aquifers of the Buffels River

	Error (%)	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
<b>Sr (µg/L)</b>													
Mar-2013	6.4	340.9	294.1	1090.1	1288.3	857.2	1580.9	10739.6	5464.3	4972.7	1845.5	832.8	
Sep-2013	2.2	326.5	345.5	1091.8	1412.0	1331.3	1711.5	11746.6	6053.1	5525.0			569.1
Feb-2014	5.1	333.5	327.8	1172.0	1474.5	1811.6		14312.2	6344.7	65.0	4075.9		
<b>Mn (µg/L)</b>													
Mar-2013	9.9	34.1	62.9	44.1	143.2	543.0	7.1	2922.9	2279.8	54.2	225.0	118.2	
Sep-2013	2.7	31.4	72.7	20.0	108.8	95.9	7.0	4683.5	2774.9	9345.5	9275.9	5.5	19.1
Feb-2014	3.3	124.4	32.4	68.3	147.2		65.3	1284.4	2978.9	318.5	273.7		
<b>Fe (µg/L)</b>													
Mar-2013	1.1	4.7	33.2	48.0	874.0	300.8	<1.841	2.9	1509.1	<1.841	9.8	4.8	
Sep-2013	6.4	29.1	168.5	45.3	4770.5	38.0	45.4	14.4	29033.5	31845.4	32126.8	19.1	0.7
Feb-2014	6.6	638.6	4.9	128.2	4486.9	106.3		4.7	15634.6	1355.2	37.8		
<b>Ni (µg/L)</b>													
Mar-2013	9.9	1.0	3.0	5.1	6.1	17.1	<0.382	8.4	0.7	13.4	2.8	1.3	
Sep-2013	5.0	0.5	1.8	0.1	3.2	3.4	0.1	4.0	0.9	254.9	259.7	0.7	14.1
Feb-2014	3.2	1.7	1.4	0.7	4.8	1.1		5.9	0.7	11.2	3.6		
<b>Cu (µg/L)</b>													
Mar-2013	0.6	2.6	1.3	2.8	<0.393	2.3	0.7	7.1	0.5	15.3	9.8	9.3	
Sep-2013	3.3	1.1	1.1	4.3	0.6	9.5	0.9	4.3	9.5	17559.6	17474.8	14.1	3.2
Feb-2014	2.7	0.8	1.6	7.5	17.4	1.4		7.4	0.8	1674.0	7.0		

### 2.4.3 Isotopes

#### 2.4.3.1 Oxygen and Hydrogen Isotopes

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values for all the samples across the three sampling seasons are given in Table 2.6. The  $\delta^2\text{H}$  isotopes range from -18.2 to -5.6 ‰, -16.1 to -1.9 ‰ and -17.8 to -0.9 ‰ respectively for the three sampling seasons. Sample S07 is more enriched in heavy  $\delta^2\text{H}$  isotopes than all the other groundwater samples in the study. There is no temporal variation in the  $\delta^2\text{H}$  values of the groundwater samples measured during the wet season and those measured during the dry seasons. The  $\delta^{18}\text{O}$  isotopes range from -3.82 to -0.13 ‰, -3.70 to 0.14 and -3.40 ‰ to 0.99 ‰ respectively for the three sampling seasons. Similarly, sample S07 was enriched in heavy  $\delta^{18}\text{O}$  isotopes. The  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  relations of groundwater against the Local Meteoric Water Line (LMWL) and the Global Meteoric Water Line (GMWL) for the three sampling seasons are shown (Fig. 2.11), and they indicate an evaporative trend. The groundwater samples from all the three sampling campaigns show slopes of 4-5 on the plotted  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  relations. There is no correlation between EC and  $\delta^{18}\text{O}$  for the groundwater samples (Fig. 2.12). Groundwater samples far from the coast are more depleted in heavy isotopes as compared to those close to the sea, with the exemption of B03, the borehole used for livestock at Buffelsrivier.

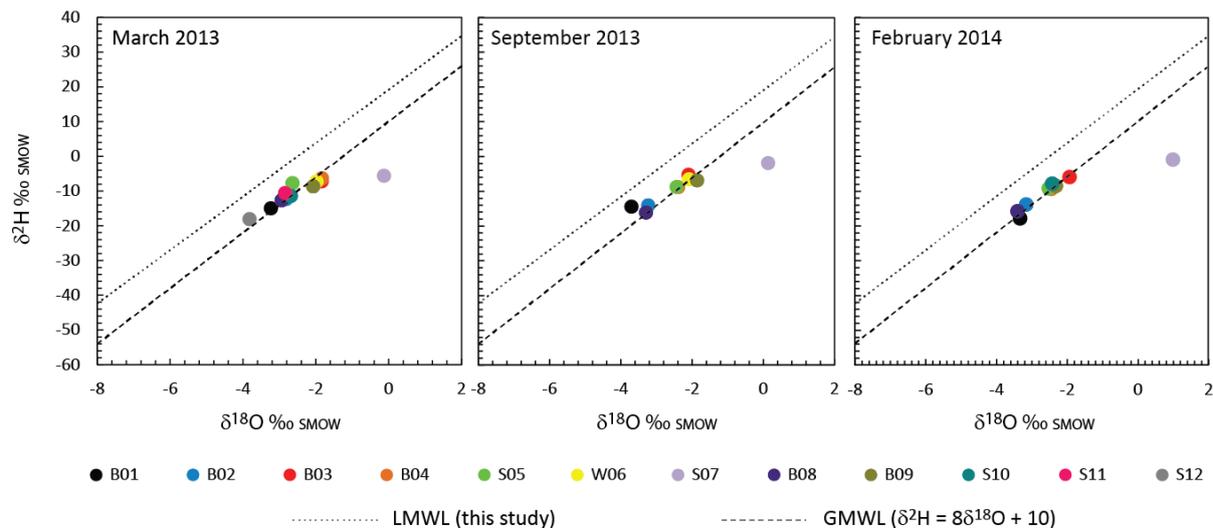


Figure 2.11: The stable isotopes of the individual groundwater samples

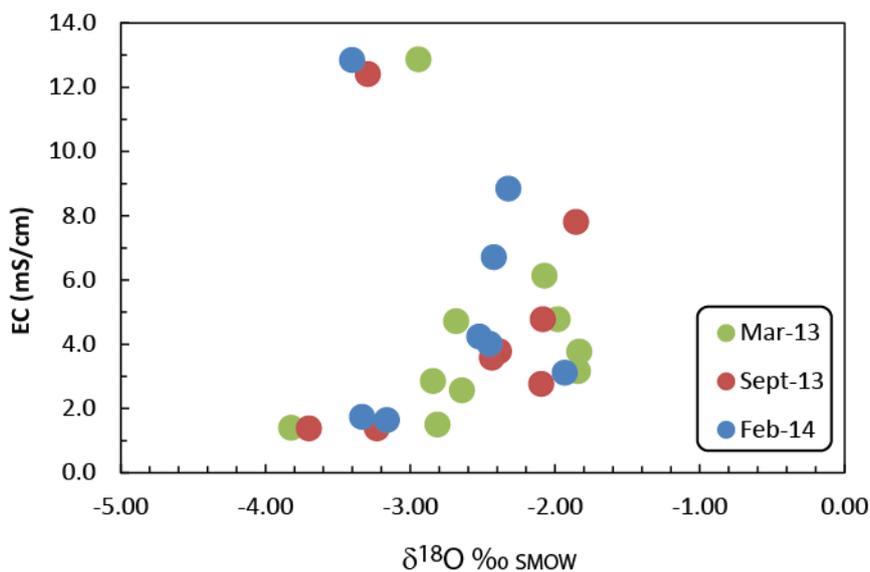


Figure 2.12: EC-  $\delta^{18}\text{O}$  relationship of the groundwater samples

Table 2-6: Stable isotopes of the groundwater samples

	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
$\delta^{2}\text{H} \text{‰}$												
Mar-2013	-14.7	-12.3	-7.2	-6.3	-7.8	-7.3	-5.6	-12.7	-8.7	-11.4	-10.6	-18.2
Sep-2013	-14.5	-14.0	-5.2	-8.8	-8.8	-6.6	-1.9	-16.1	-6.9			
Feb-2014	-17.8	-13.8	-5.9	-9.3	-9.2		-0.9	-15.8	-8.5	-7.8		
$\delta^{18}\text{O} \text{‰}$												
Mar-2013	-3.23	-2.81	-1.84	-1.83	-2.64	-1.98	-0.13	-2.94	-2.07	-2.68	-2.84	-3.82
Sep-2013	-3.70	-3.23	-2.09	-2.39	-2.43	-2.08	0.14	-3.29	-1.85			
Feb-2014	-3.33	-3.16	-1.93	-2.45	-2.52		0.99	-3.4	-2.32	-2.42		

#### 2.4.3.2 <sup>87</sup>Sr Isotopes

The measured Strontium-87 samples are given in Table 2.7, given as <sup>87</sup>Sr/<sup>86</sup>Sr ratios. The <sup>87</sup>Sr was then calculated using the measured strontium concentrations tabulated in Table 2.5. Strontium isotopes were only analysed in the groundwater samples taken in February 2014. The Sr concentrations and <sup>87</sup>Sr/<sup>86</sup>Sr ratios ranged from 0.1 mg/L (B09) to 14.3 mg/L (S07) and from 0.72225 (S07) to 0.74740 (B03), respectively (Tables 2.4 and 2.6). The highest Sr concentrations correspond to the lowest <sup>87</sup>Sr/<sup>86</sup>Sr ratios which are found in groundwater sample (S07). However, there is lack of correlation between the 1/Sr concentrations and their corresponding <sup>87</sup>Sr/<sup>86</sup>Sr ratios (Fig. 2.11).

#### 2.4.3.3 <sup>36</sup>Cl Isotopes

The <sup>36</sup>Cl/Cl ratio ranges from 21-162.5×10<sup>-15</sup> (Table 2.6), and were all measured at an error of less than 10%. Sample W06 has the highest ratio, while the lowest ratio was measured at B02. Similarly, <sup>36</sup>Cl was calculated using the measured chloride concentrations in the groundwater. Plots of <sup>36</sup>Cl and Cl concentration as well as <sup>36</sup>Cl/Cl and Cl were used to determine the salinity sources to the groundwater. There is no correlation between <sup>36</sup>Cl and Cl (Fig. 2.12 and 2.13).

#### 2.4.3.4 Tritium

Tritium values were obtained on borehole water samples measured in February 2014. The measured tritium concentrations in these groundwater samples are consistently very low and range from 0.4 to 1.3 TU (Table 2.6). The highest tritium concentration was measured at B01 and the lowest at B02. There is no systematic spatial variation in the tritium values along the course of the Buffels River. The recharge periods (groundwater age) of the groundwater samples were identified by comparing the tritium contents in the groundwater with those of the present day rainwater. Since no tritium analysis were done on the rainwater from this study, groundwater age of the alluvial aquifers were determined based on the rainwater tritium contents from southern Africa from Talma and van Wyk (2013) (Fig. 2.15).

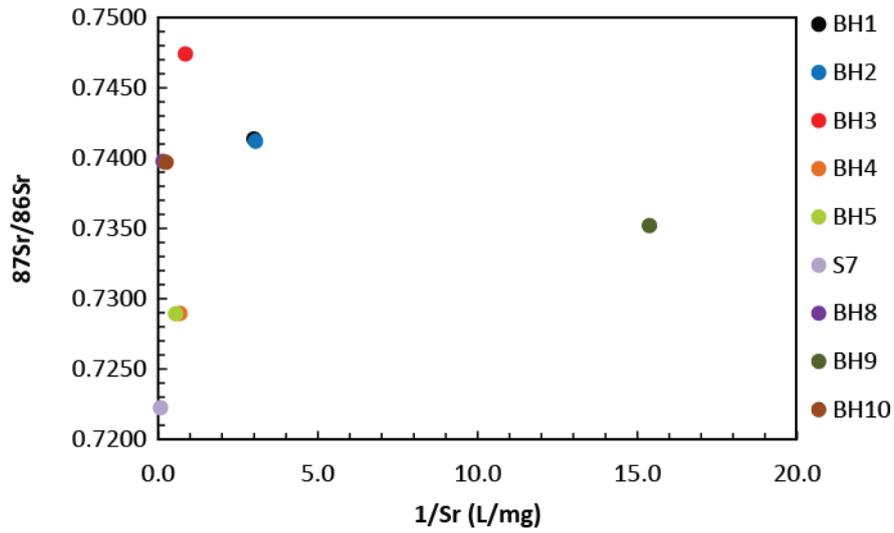


Figure 2.13:  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio plotted against  $1/\text{Sr}$

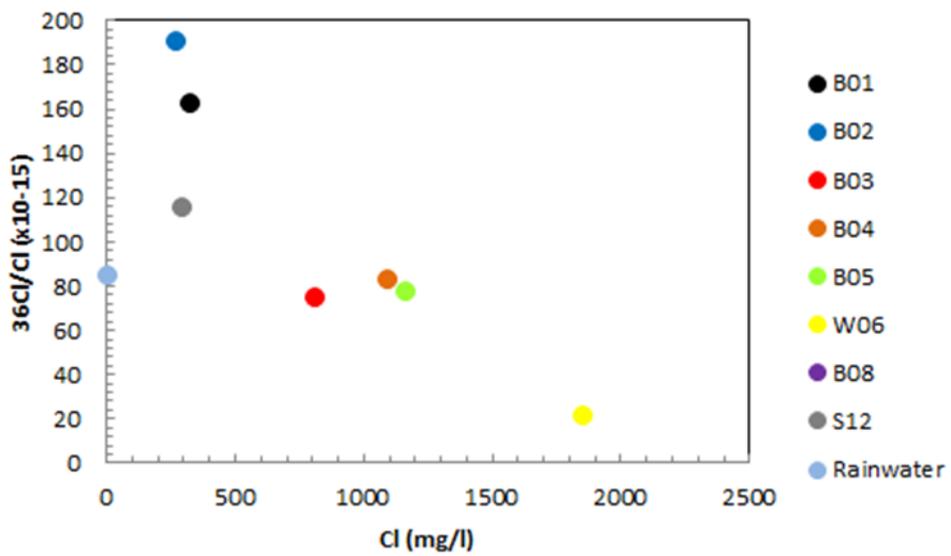


Figure 2.14: The  $^{36}\text{Cl}/\text{Cl}$ -Cl relationship of the groundwater samples

Table 2-7:  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{36}\text{Cl}/\text{Cl}$  and tritium activities for the alluvial aquifers along the Buffels River

Sample ID	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{s}$ internal	$^{36}\text{Cl}/\text{Cl}$ ( $\times 10^{-15}$ )	Error	$^3\text{H}$ (TU)	Error
B01	0.74135	16.0	162.5	6	0.4	$\pm 0.2$
B02	0.74119	14.5	189.9	7	1.5	$\pm 0.3$
B03	0.74740	16.4	74.2	3.4	0.5	$\pm 0.2$
B04	0.72895	13.8	83.1	3.8	1.3	$\pm 0.3$
S05	0.72892	14.2	77.0	3.5		
W06			21.0	1.4		
S07	0.72225	11.7				
B08	0.73976	12.2	124.3	4.9	1.1	$\pm 0.3$
B09	0.73519	19.2				
W10	0.73971	11.1				
W11						
S12			114.9	4.4		
Rainwater			84.9	3.9		

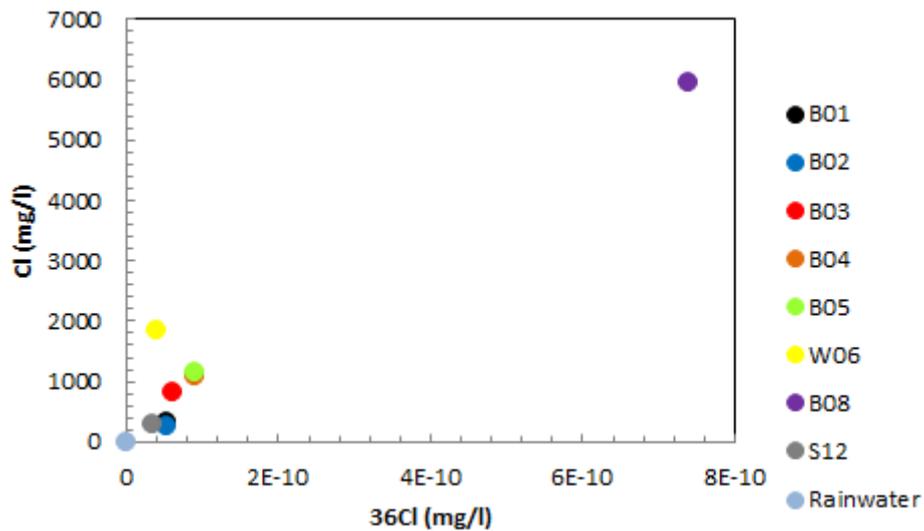


Figure 2.15:  $^{36}\text{Cl}-\text{Cl}$  concentrations relationship

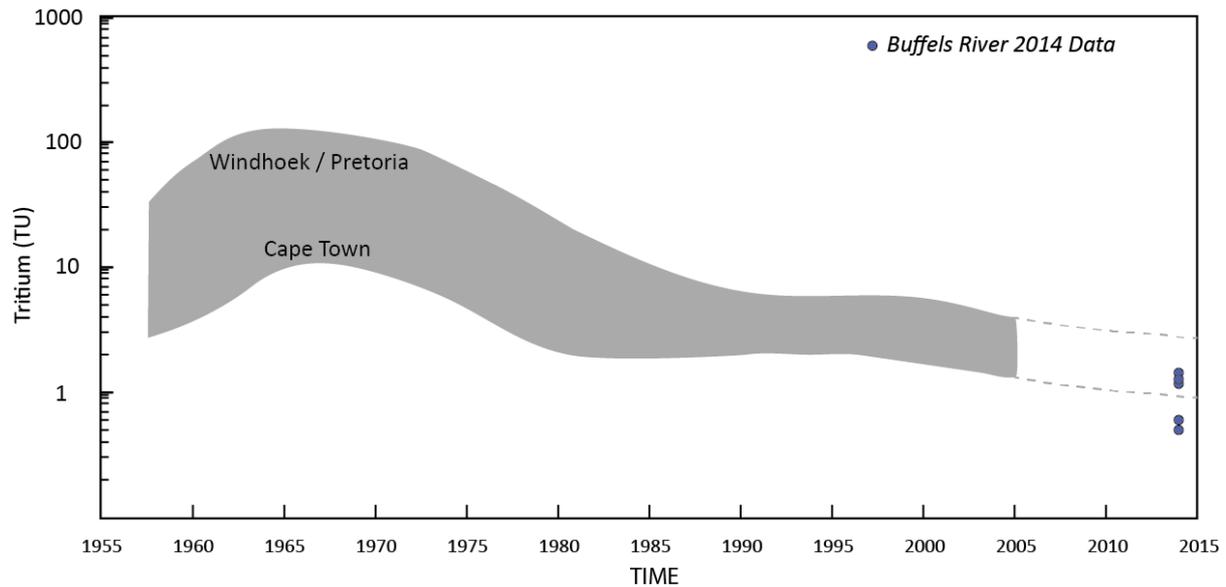


Figure 2.16: Time series of tritium analyses from the sub-continent since 1958 (from Talma and van Wyk, 2013) with the 2013-2014 groundwater samples from the Buffels River.

## 2.5 Discussion

### 2.5.1 Characterisation of Buffels River Shallow Groundwater

The piper plots and stiff diagrams (Fig. 2.7 and 2.8) were plotted based on the major cations and anions, and are used to understand the groundwater evolution in the study area. The dominant water type for the sampled groundwater in all three sampling campaigns was Na-Cl, as a result of the dominant  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the groundwater. Adams et al (2004) and Leshomo (2011) also observed the same groundwater character in other areas of Namaqualand. The source(s) of the dominant chloride ions are discussed in the next section. There is a linear correlation between Cl and Na for the groundwater samples taken in 2013, pointing to a similar source. Non-linear relationships were observed in samples taken in February 2014, and this is attributed to analytical machine errors involved with the changes of IC machines used for the analysis of anions. Groundwater with a Na- $\text{HCO}_3$  character was identified for the samples B02 and S12 during the March 2013 sampling season. This has been attributed to the weathering of silicates. Groundwater sample B09 also had a Na- $\text{SO}_4$  water character in February 2014. This is a result of removal of chlorides from water as the borehole water is treated to be suitable for human consumption at the mine.

The groundwater age of the alluvial aquifers along the Buffels River is relatively young with respect to the atmospheric bomb testing tritium decay. Only two boreholes have tritium activities less than 1 TU (Table 2.6). The samples measuring tritium decay less than one TU are a mixture of recent recharged rainwater and old groundwater recharged prior to the bomb test. Groundwater ages determined by tritium are not necessarily the true age of the groundwater, therefore considered apparent ages (Price et al., 2003). Previous studies by Adams et al., (2004) also indicated using  $^{14}\text{C}$  that the alluvial aquifers host the most recently recharged water.

### **2.5.2 Spatial and Temporal Variations in Salinity**

The salinity is highly variable in the alluvial aquifers, where high EC and chloride concentrations were measured in samples taken from the lower catchment of the Buffels River as compared to the samples taken from the upper catchment. High concentrations of ions mainly  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were measured in groundwater samples taken close to the mining activities (B04, S05, S07 and B08). The high concentrations are attributed to the additional constituents to the groundwater from the mining activities. In addition to these, groundwater samples in close proximity show different chemical compositions. This is shown in the hand dug wells W10 and W11, which are less 100m apart but have different chemical compositions. The different chemical compositions in nearby groundwater wells indicate that the aquifers are disconnected. Similar variations were reported by Adams et al., (2004) in central Namaqualand.

Temporally, there is a decrease in the electrical conductivity and chloride concentration of the groundwater in the wet season, as compared to the dry seasons, with the exemption of S05. The high salinities during dry seasons are attributed to the concentration of minerals by evaporation. Recharge by fresh rainwater during the wet season dilutes the groundwater resulting in low salinities. Sample S05 is the hand augered groundwater sample taken near the mine pump at Kleinzee De Beers Mine in close proximity to the membrane. The increase in the chloride concentration after rain can be attributed to the accumulation of chloride by the membrane, but further studies need to be done to verify these.

### **2.5.3 Source(s) of Salts**

The objective of this research was to determine the source(s) of salt-loads to the alluvial aquifers along the Buffels River catchment. The salt-loads in these shallow alluvial aquifers are high, and reach higher levels whereby boreholes are abandoned for both human consumption and livestock use. The source(s) of the solutes is not known, and can be from one source or from a combination of sources. The chemical composition of groundwater indicates the dominance of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions resulting in a sodium chloride water type. There is no correlation between chloride concentration and  $\delta^{18}\text{O}$  value in the groundwater samples ( $r^2=0.0163$ ) (Fig.2.12), and this points to multiple salinity sources to the alluvial aquifers (Hamouda et al., 2011). The multiple salinity sources are further shown by a good correlation between the major element concentrations (i.e. Na, Ca, Sr, Mg,  $\text{SO}_4$  and K) and chloride concentration (Fig. 2.13) (Nencetti et al., 2005).

Precipitation in Namaqualand has low chemical concentrations, with dominant Na and Cl ions evaporated from the ocean, as the region is in close proximity to the coast (Adams et al., 2004). The rainwater samples taken in this study show very low Cl concentrations, with the highest chloride concentration of 22mg/L measured in rainwater from coastal town of Kleinzee. The chloride concentrations in groundwater are very high, and this indicates the chlorides in the groundwater are not entirely of meteoric origin. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes of the groundwater samples show an

evaporative trend with respect to the LMWL (Fig. 2.11), indicating that groundwater has been evaporated prior or during infiltration. Evaporation removes water and concentrates the dissolved chemical constituents in the residual water, resulting in high salt-loads in the alluvial aquifers. Correspondingly, high evaporation rates in comparison to the precipitation rates have been reported by earlier researchers in Namaqualand as a potential source of groundwater salinity in the region (Adams et al., 2004; Leshomo, 2011). Studies from other arid and semi-arid environments also indicate evaporative concentration as the dominant salinity source in these environments (Scanlon et al., 2002).

Generally, salinity from evaporative concentration is indicated by a strong correlation between  $\delta^{18}\text{O}$  and Cl (Allison et al., 1990). However, there is no correlation between  $\delta^{18}\text{O}$  and Cl concentration in the groundwater samples, and this is attributed to transpiration effects by the vegetation along the river. Transpiration does not fractionate stable isotopes (Allison et al., 1990). The lack of correlation is prominent after the rain season (September 2013), indicating the presence of plants. Moreover, evaporation increases concentrations of both Cl and  $^{36}\text{Cl}$  in water (Cresswell et al., 1999). A similar trend is observed in these groundwater samples (Fig. 2.15), with the exemption of sample W06. Therefore, evaporation is a potential source of the high salt-loads in the alluvial aquifers along the Buffels River.

The groundwater samples have high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, with an average of 0.73608. High  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are produced by igneous rocks that contain Sr-bearing minerals such as K-feldspar, hornblende and micas (Clarke and Fritz, 1997). The chemical composition of the Rietberg Granites of the Spektakel Suite in the Bushmanland Subprovince (the Buffels River is in the Bushmanland Subprovince) also shows high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Clifford et al., 1975), which are in the same ranges as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the groundwater samples. The high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are indicative of water-rock interactions and the high salt-loads in the groundwater are therefore derived from the dissolution of the rock mass. There is no correlation relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $1/\text{Sr}$  concentrations in groundwater (Fig.2.13), indicating that there are multiple sources of Sr, to the groundwater.

Earlier studies in Namaqualand recorded high sulphate concentrations in the groundwater, and these were derived from the pegmatite (Leshomo, 2011). High sulphate concentrations are also recorded in this study and there is a strong correlation between chloride and sulphate in the groundwater samples (Fig. 2.10), indicating the two anions have a similar source. The groundwater samples also have high Na concentration, which earlier studies reported to be derived from the dissolution of granites and gneisses in the region (Hohne and Hansen, 2008). However, there are no chloride concentration studies done on the lithology to quantify the exact chloride derived from these granites.

High EC values are recorded in boreholes in close proximity to the mining areas (i.e. S07 and B08) as compared to those taken away from the mining activities (i.e. B01 and S12). This localised high salt loads points out to an anthropogenic salt-source, pointing at salinisation from the mining wastes. The groundwater close to the mining areas further shows high ion concentrations, with dominant chloride

and sulphate anions. Sulphate is the significant parameter that indicates mining activities influence on groundwater (Hansen and Hohne, 2008). Therefore, the mining activities also contribute to the salt-loads, but this needs further research.

## 2.6 Conclusion

The main aim of the study was to determine the source(s) of salt-loads to the shallow alluvial aquifers of the Buffels River. The geochemical analyses (mainly the ionic ratios) and the isotopic analyses of  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^{36}\text{Cl}$  and  $^{87}\text{Sr}$  were used in determining these salt sources. Salinisation of the groundwater system is from a combination of sources and this is shown by poor correlations between  $\delta^{18}\text{O}$  and Cl concentration in the groundwater.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the groundwater are very high and in the same range as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Spektakel Suite. This indicates water-rock interactions in the groundwater system. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes shows an evaporation trend. This was further shown by the  $^{36}\text{Cl}/\text{Cl}$  and  $^{36}\text{Cl}$  plot indicating groundwater was evaporated prior or during infiltration. Salinisation to the alluvial aquifers along the Buffels River is therefore from the dissolution of rock mass and the concentration by evaporation. In addition to this, there is also contribution of salts from the mining activities along the river.

### Chapter 3: Assessing recharge to the alluvial aquifers

NOTE: This material to be developed into a manuscript as follows:

Nakwafila, A.N., Miller, J.A., and Clarke, C.E., Assessing recharge rates to the alluvial aquifers along the Buffels River, Northern Cape Province, South Africa. Target Journal: Journal of hydrology

#### Abstract

Recharge studies are important in both groundwater resource management as well as water quality assessment. It is critical to determine groundwater recharge in semi-arid environments due to the water scarcity and poor groundwater quality problems in these environments. In this study, recharge rates and mechanisms to the alluvial aquifers along the Buffels River in Namaqualand were determined to help understand salt sources contributing to salinisation of the groundwater. The alluvial aquifers are recharged by the infiltration of rainwater and occasional floodwater. The recharge mechanisms to the alluvial aquifers were determined using the stable isotopes of  $^{18}\text{O}$  and  $^2\text{H}$  by determining whether recharge was direct or indirect. The chloride mass balance (CMB) method was used to estimate the recharge rates. The groundwater samples show an evaporative trend, which is indicated by fractionated  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  stable isotopes. In estimating recharge rates, the CMB method assumes atmospheric chloride is the only source of chloride to the groundwater. However, there is additional chloride to the alluvial aquifers in this study derived from the aquifer lithology rock mass dissolution. Low recharge rates of 0.1 mm/a were estimated at the coastal town of Kleinsee, and the alluvial aquifers inland at Buffelsrivier had higher recharge rates with the maximum of 3.4 mm/a, which is 0.1-2.1% of the annual precipitation. A simulation model was run to detect how many percentages of annual precipitation in the region is recharged to yield the measured chloride concentrations in groundwater. This was found to be 1-5% of annual precipitation. Therefore, additional non-atmospheric chloride underestimates estimated recharge rates to the alluvial aquifers. However, the CMB method still gives significant recharge rates estimates, but inaccurate and needs to be supported by another recharge estimating method.

**Key Words:** Groundwater, Alluvial aquifers, Namaqualand, Semi-arid regions, Stable isotopes

### 3.1 Introduction

Understanding the groundwater balance in a groundwater system is important for both groundwater resource management and contamination studies. The groundwater balance is defined by the general hydrologic equation, which states that groundwater recharge is equal to discharge minus changes in storage (Freeze and Cherry, 1979). Groundwater recharge is defined as the sum of all the inputs to the hydrological budget, while discharge is the sum of all the outputs from the hydrological budget (Conrad et al., 2005). In general the groundwater recharge is much harder to constrain than the groundwater discharge. This is because whilst discharge from a groundwater system can be directly measured, recharge is usually just estimated or calculated based on various assumptions. As a result a large number of methods have been formulated for estimating groundwater recharge (Gee and Hillel, 1988; Simmers 1988, 1997; Lerner et al., 1990; Allison et al., 1994). These have been divided into physical and chemical methods. The physical methods (i.e. lysimeters, water balances, and water table fluctuations) measures recharge at specific moments and/or locations (Scanlon et al., 2002). Chemical methods estimate recharge based on the distribution of a tracer (i.e.  $^2\text{H}$ ,  $^3\text{H}$ ,  $^{18}\text{O}$  and  $\text{Cl}$ ) (Allison, 1987). The method in which recharge is calculated for a given system depends on the nature of the environment being considered.

Arid and semi-arid environments are usually strongly dependent on groundwater due to the general lack of surface water. The rate of groundwater recharge in these environments is therefore a critical parameter to quantify. However, groundwater recharge rates are more difficult to quantify in arid and semi-arid environments (Verma, 1979; Simmers, 1988), particularly the use of physical recharge estimation methods which are prone to significant uncertainties because of the episodic and highly variable nature of precipitation in these environments (de Vries and Simmers, 2002; Subyani, 2004; Lerner et al., 1990; Sophocleous, 1992). Chemical recharge estimation methods are advantageous for use in arid and semi-arid environments because the tracers are usually conservative and concentrations represent spatially uniform inputs to the soil surfaces and groundwater system (Lerner et al., 1990).

The chloride mass balance (CMB) method (Eriksson and Khunakasem, 1969) is often used in recharge rate approximation due to its relatively low cost and time integrating properties. Chloride is a conservative tracer with high solubility characters and is easily measurable (Allison and Hughes, 1978). Although chloride is a chemical tracer, it has an advantage over other tracers because it conserves the atmospheric inputs during the recharge process, which allows a physical mass balance approach to be used (Dettinger, 1989; Edmunds and Gaye, 1994). It has therefore been widely applied in a range of different environments and particularly in arid and semi-arid environments. In estimating recharge rates, the CMB method assumes atmospheric chloride is the only source of chloride to the groundwater system (Eriksson and Khunakasem, 1969). However, in arid and semi-arid environments, salinisation of groundwater is often a common problem and complicates the application of the CMB method. If the salinisation is the result of evaporative concentration then the CMB is still usable with some additional constraints. However, if the salinisation is the result of

addition of salts from other sources, for example sea-water ingress in coastal aquifers or dissolution of rock salts, then the application of the CMB method is harder to justify because a mass balance between rainfall recharge and chloride in the groundwater no longer exists.

In Namaqualand of the Northern Cape Province, South Africa, there are two types of aquifers, the shallow alluvial aquifers and deep crystalline aquifers, both of which are variably saline. The salts are thought to come from the dissolution of rock mass (Chapter 2) and further concentrated by evaporation processes. The shallow alluvial aquifers, within alluvium deposits of the ephemeral rivers, are typically recharged by direct infiltration of precipitation and by flooding (Benito et al., 2010). The additional chloride in the groundwater not contributed by precipitation results in underestimated recharge rates to these alluvial aquifers. Furthermore, recharge rates to the alluvial aquifers are given on an annual basis but recharge only occurs after significant rainfall or flooding and not after every rainfall event (Adams et al., 2004). The chloride mass balance method also has short comings for it does not effectively capture seasonal effects, annual dynamics, or other short-duration events responsible for episodic recharge (Ng et al., 2009). Therefore recharge rates calculated using CMB need to be interpreted with caution.

Previous recharge rates in Namaqualand were calculated using the CMB method as well as saturated volume fluctuations (SVF) and cumulative rainfall departures (CRD) by Adams et al., (2004). The rates obtained varied between 0.1 – 10 mm/yr. The CMB method was found to be useful but needed to be supported and strengthened by other means of estimating or calculating recharge. Although the salts were not considered to be a major complicating factor with the CMB method, this assumed that the additional chloride is coming from evapotranspiration and not from dissolution of other salt sources. In this study, the CMB method for calculating recharge in the Buffels River is revisited. Recharge rates are calculated using decadal rainfall data and a range of chloride concentrations in the precipitation. These values are then compared to previous estimates of recharge and their validity discussed. The role of salt dissolution is then assessed to see how it impacts on the calculated rates.

### **3.2 The Study Area**

The study was done on the alluvial aquifers along the Buffels River in Central Namaqualand. Groundwater samples were collected along the river, from the intersection of the N7 national road with the Buffels River down to the coastal town of Kleinzee where the river drains into the Atlantic Ocean (Fig. 3.1). According to DWAF (2002), the selected catchment is in the western part of the Lower Orange Water Management F30. It is bounded by S29°59.523'-S29°39.209' and E017°52.473'-E017°04.651'. The Buffels River is the largest ephemeral river in Namaqualand, with a drainage area of approximately 9250km<sup>2</sup>. In general, recharge to groundwater is influenced by the geology, climate, geomorphology and the soils of the region (Adams et al., 2004), and these characteristics are described below for the Namaqualand region:

### **3.2.1 Geology**

The geology of the area controls the flow paths within the aquifer system. The Buffels River is located within the Namaqua Metamorphic Province (NMP) of the Namaqua-Natal Belt. The basement rocks in Namaqualand comprise of the Pre-Gondwana rocks (Theart 1980). These were intruded by the granites and gneisses of the Namaqualand Metamorphic Complex (Clifford et al., 2004). The NMP is subdivided into four subprovinces namely the Richtersveld, Bushmanland, Gordonias and Kheis Subprovinces (Blignault et al., 1983; Hartnady et al., 1985). The Buffels River catchment drains through the Bushmanland Subprovince, which consists of deformed orthogneisses and biotite-bearing granitic intrusions (Waters, 1990). These rocks are metamorphosed to medium-high grades attaining maximum metamorphic conditions of amphibolite and granulite facies (Jacobs et al., 1993). The Buffels River catchment bedrock comprises of impermeable meta-sedimentary rocks, basic granites and ultrabasic intrusive rocks, of the Aggeney, Okiep, Steinkopf and Garies Terranes (Marais et al, 2001). The detailed geology context is given in Chapter 1 (Section 6.1).

### **3.2.2 Climate**

Namaqualand's climate is semi-arid to arid, with two different rainfall seasons. The region on the west toward the coast receives winter rainfall while eastern Namaqualand receives rainfall during summer (Adams et al., 2004). The study area is within the winter rainfall zone, and precipitation results from the frontal convections from the Atlantic Ocean (Benito et al., 2010). In addition to this, cyclonic rainfall caused by the movement of mid-latitude cyclone systems inland over the south west coast are also common within the winter rainfall zone (Benito et al. 2010). Higher mean annual precipitation rates are recorded in the mountainous areas of Namaqualand with 480mm recorded at Kamies Mountains, and this is caused by the orographic effects (Adams et al., 2004). The lowest annual precipitation amounts of 88mm were recorded at Kleinzee by the west coast for the period of January 1984-December 2012; resulting from the cold Benguela current effects, which cause less moisture over the West Atlantic Ocean coast (Benito et al., 2010). Precipitation varies considerably spatially and temporally in the region. Air temperature ranges from a minimum of 2 degrees Celsius in winter to a maximum 45 degrees Celsius in summer (South African Weather Bureau, 2013). The annual evapotranspiration is reported to be 12 times more than precipitation amount (Adams et al., 2004). The region has sparsely vegetation landscapes, dominated mainly by grass, shrubs as well as some occasionally succulents (Hohne and Hansen, 2008). Groundwater losses through transpiration in the lower Buffels were estimated to reach 19,000 m<sup>3</sup> per day (Cornelissen 1968).

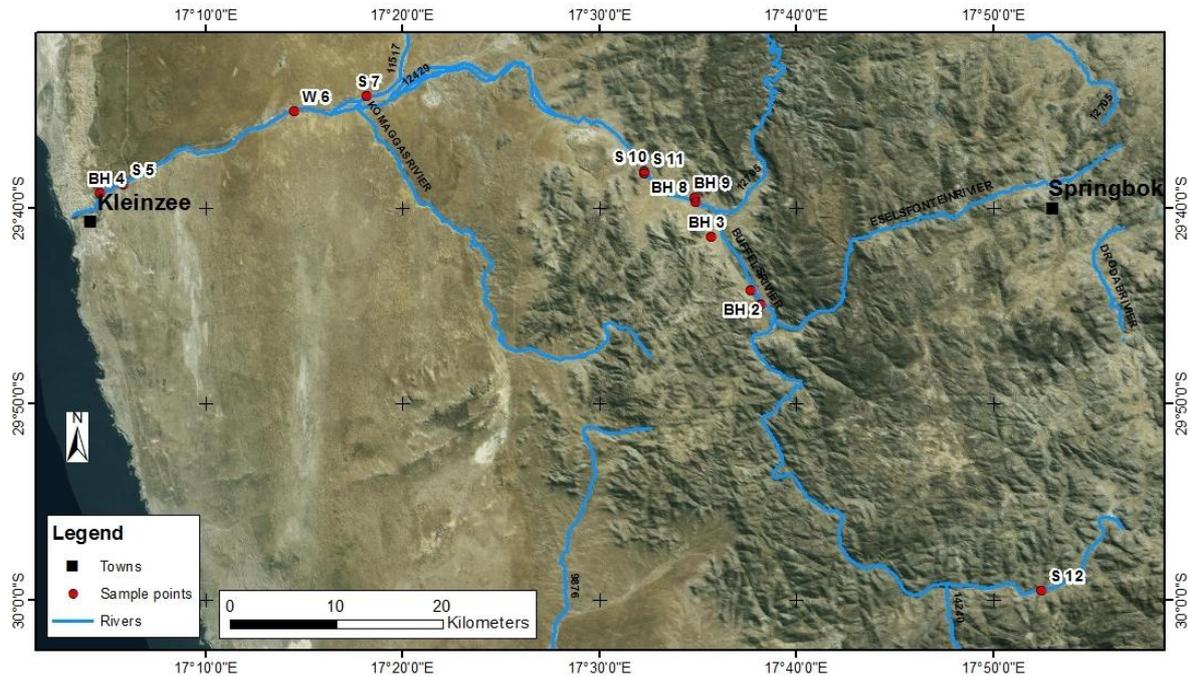


Figure 3.1: Distribution of the sampled groundwater locations from the N7 National road to Kleinzee

### 3.2.3 Geomorphology

Topography is the most significant factor driving both surface water and groundwater flow (Adams et al., 2004). It has an impact on the amount of rain water that infiltrates through to the groundwater. The topography in Namaqualand varies from a very low altitude and relief coastal zone to a high altitude escarpment zone. Namaqualand is characterised by three geomorphologic regions, namely the coastal lowland, an escarpment zone and the Bushmanland Plateau (Adams et al., 2004), resulting from previous geomorphic cycles in the region (Partridge and Maud, 1987). The coastal lowlands are covered by recent sands and underlain by the crystalline basement rocks. The escarpment zone is characterised by exposed domes of granite gneisses, weathered materials from the granite gneisses which are going up to depths of 54-60m, fractured rocks as well as alluvium filled valleys (Adams et al., 2004).

### 3.3 Chloride Mass Balance Method

The CMB method is based on tracing the geochemical signals from precipitation and from the unsaturated zone solutions into the groundwater. It is efficient in estimating recharge in arid and semi-arid regions (Diouf et al., 2013). When determining recharge using the chloride mass balance method, it is assumed that atmospheric chloride (both dry and wet depositions) is the only source of chloride to the groundwater and contributions from other sources such as human activities and weathering are neglected (Dettinger, 1989). The recharge estimates are therefore based on the mass balance between atmospheric chloride (wet and dry depositions), surface runoff, the unsaturated zone (soil

matrix) and groundwater (Klock, 2001). For studies in Namaqualand, the surface runoff component is neglected due to lack of surface runoff chemical information (Adams et al., 2004).

A number of studies in southern Africa have shown that dry deposition of chloride is negligible as it is too small (>0.1mg/L) compared to the wet deposition (0.4-1.1mg/L) (Külls, 2000; Klock, 2001). Therefore, in areas with no geological chloride sources, recharge is obtained by balancing the chloride flux in the soil column with the outflow at the bottom of the root zone (Klock, 2001). The mass balance method of estimating the rate of water movement relates the mass of the tracer in the unsaturated zone to the rate at which the tracer arrives at the surface, assuming that the chloride uptake by plants is negligible. This is illustrated by the equation:

$$R = \frac{P * Cl_p}{Cl_{sw}} \quad \text{Equation 1}$$

Where R (mm/a), P (mm/a),  $Cl_p$  (mg/l) and  $Cl_{sw}$  (mg/l) are groundwater recharge, mean annual precipitation, chloride concentration in precipitation and chloride concentration in the soil water of the unsaturated zone.

The chloride mass balance method is also applied to the saturated zones, where chloride content in groundwater is used instead of considering chloride in the soil water of the unsaturated zone. This is represented by the equation:

$$R = \frac{P * Cl_p}{Cl_{gw}} \quad \text{Equation 2}$$

Where R (mm/a), P (mm/a),  $Cl_p$  (mg/l) and  $Cl_{gw}$  (mg/L) are groundwater recharge, mean annual precipitation, chloride concentration in precipitation and chloride concentration in the groundwater, respectively. The groundwater samples used in this study were obtained from the saturated zone; therefore Equation 2 is used in the estimation of recharge in this study.

### **3.4 Materials and Methods**

#### **3.4.1 Field Sampling**

Groundwater samples were taken from the shallow aquifers lining the Buffels River. The upstream sample was taken at the intersection of the Buffels River with the N7 national road, and samples were collected downstream till Kleinzee on the coast (Fig.3.1). A total of 31 groundwater samples were taken on three sampling campaigns. These were undertaken in early March 2013 before the wet season, in September 2013 after the wet season and in February 2014 again before the wet season. The two last seasons (September 2013 and February 2014) resampled the sites sampled in the first season. However, not all sampling sites could be sampled each time. Heavy rain during the winter of 2013 washed out two of the hand dug wells that were sampled during the summer of 2013. These were reinstated by the third sampling round in the summer of 2014. Groundwater was also not found at some of the hand augured sites during summer samplings. Table 1 (Chapter 2) gives a summary of

samples taken for each sampling season. Samples were taken from existing hand dug wells and boreholes, mainly used for domestic, livestock and irrigation purposes. A monitoring borehole at the Spektakel Mine was also sampled. In cases where boreholes and hand dug wells were not available, groundwater was accessed through shallow bucket augured holes. The boreholes were pumped until the groundwater measurements of the EC and pH were stable before sampling. Samples from the hand dug wells and the hand augured sites were taken directly using a bailer and no pre-sampling pumping was done. For each site chloride and stable isotopes samples were collected. Samples taken for chloride analyses were collected in clean 50ml conical Polypropylene (PP) tubes and for stable isotopes analyses 15ml PP tubes. Both samples were filtered through a 0.45µm cellulose acetate filter, and kept cold prior to analysis.

Temperature, pH and electrical conductivity (EC) for each site were measured in the field using an EXTECH EC500 pH/Conductivity probe. This probe was calibrated daily in the morning using the pH 4 and 7 standards and the EC 1413 µS/cm standard to verify the calibrations. The temperature readings were taken first for every site, to avoid atmospheric alterations. Alkalinity was also measured in the field by acid titration with a HACH digital titrator.

### **3.4.2 Rainwater**

Rainwater samples were collected from Naries Guesthouse which is approximately 30km west of Springbok, from the police station at Kleinzee and at Komaggas where the South African Meteorological Bureau has a monitoring station. These were collected whenever there was rain between March 2013 and April 2014 from existing rain gauges at 8am in the morning by the officials at the three stations. Samples were collected for the analyses of chloride concentration and stable isotope (<sup>18</sup>O and <sup>2</sup>H). These were collected in clean 50ml PP tubes and kept cold until collection from the stations for analyses. In addition to these, daily rainfall amounts for the specific stations were recorded. Deuterium excess in groundwater was calculated from the equation:

$$\text{Deuterium excess} = \delta^2\text{H} - 8\delta^{18}\text{O} \quad \text{Equation 3}$$

The weighted mean chloride was calculated by multiplying the daily precipitation amount (mm) with the chloride concentration in the rainwater (mg/l) for that particular day. These were calculated using the equation:

$$\sum P * Clp \quad \text{Equation 4}$$

Where P (mm) is the daily precipitation amount and Clp (mg/l) is the chloride concentration of rainwater for a specific rain event. The calculated mean weighted chloride is the one used in the estimation of recharge using CMB method. Furthermore, historical rainfall data from 1984-2012 was obtained for the South African Weather Bureau (SAWB, 2013), for Springbok, Buffelsrivier and

Kleinzee. The average annual precipitations used in the CMB calculation were then derived from these annual rainfall records (Fig. 3.2).

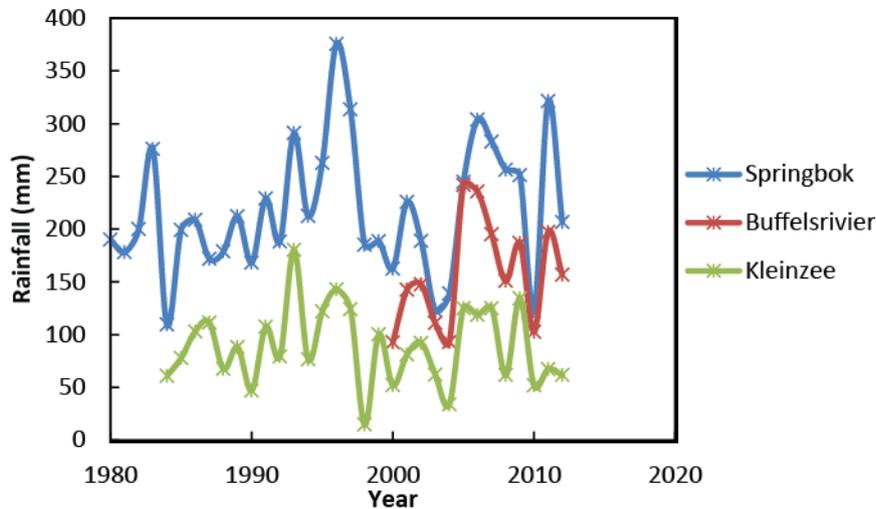


Figure 3.2: Decadal annual precipitation records for Kleinzee, Buffelsrivier and Springbok from the South African Weather Bureau.

### 3.4.3 Geochemical Analysis

The chloride samples were analysed at the Central Analytical Facility (CAF) laboratory in the department of Soil Sciences, University of Stellenbosch. Stable isotopes samples were analysed at Water Resources Centre, University of KwaZulu Natal. The samples were sent to the laboratories keeping the time between their collection and analysis minimal.

#### 3.4.3.1. Cl Concentrations

Chloride concentrations in filtered groundwater and rainwater samples were analysed using the DIONEX DX-129 Ion chromatograph for the samples collected in 2013 and using Waters 717 Autosample-conductivity detector-Agilent 1120 pump ion chromatography machine for the 2014 samples. The samples were diluted to 10X and 100X, due to high salinity levels in the groundwater indicated by EC readings. The data was corrected using a polynomial fit to four calibration standards (Spectrascan SS-028555 standards) plus a blank. Analytical errors did not exceed 10%.

#### 3.4.3.2. Stable Isotopes

The Stable isotope analyses of both rainwater and groundwater were analysed using a Los Gatos Research (LGR) DT-100 Liquid Water Isotope Laser Analyser. A set of three standards was placed in the auto-sampler tray before every 5 samples to be analysed as well as after the last 5-sample set. The standards used have been prepared by calibration against the following known standards: LGR2 ( $\delta^2\text{H}$  -117.00,  $\delta^{18}\text{O}$  -15.55), VSMOW2 (IAEA) ( $\delta^2\text{H}$  0.0,  $\delta^{18}\text{O}$  0.0) and IA-RO53 (IAD) ( $\delta^2\text{H}$  -61.97,

$\delta^{18}\text{O}$  -10.18). Each sample and standard was sub-sampled and analysed 6 times. The standard deviation of the  $^2\text{H}$  results was less than 1.5permil and for the  $^{18}\text{O}$  samples, less than 0.3 permil (‰). The analyser gave the values as  $^2\text{H}/\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios. These ratios are then converted to  $\delta$  using the standard isotope equation:

$$\delta = \frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}} \times 1000 \quad \text{Equation 5}$$

Where  $R_{\text{sample}}$  is the ratio of the heavy to the light isotope measured for the sample and  $R_{\text{std}}$  is the equivalent ratio for the standard.

### **3.4.4 Groundwater Recharge Calculations**

Recharge to the groundwater was calculated using the CMB method (equation 2) on every groundwater sample as shown in Table 3.6. The mean annual rainfall at Kleinsee from 1984-2012 is 88.5mm, while the mean annual precipitation at Buffelsrivier from 2000-2012 is 157.9mm and the mean annual rainfall for Springbok from 1980-2012 is 217.1mm (SAWB, 2013). The average weighted chloride for the rainwater collected at Naries Guesthouse was 5.9 mg/l and this was used to represent the Buffelsrivier rainwater chloride concentrations. As only rainwater at Naries Guesthouse were analysed for chloride, rainfall chloride concentrations for Springbok and Komaggas measured by Adams et al. (2004) were adopted for sample B12 at N7 and samples taken at or near Kleinsee.

A simulated model was run to estimate the percentages of annual precipitation that are recharged to the groundwater, to get the current chloride concentrations measured in groundwater. The annual precipitations used were the same as those used in the CMB method. Chloride concentrations of 5mg/l and 20mg/l were used as chloride concentration in the rainwater, having two simulations run separately.

## **3.5 Results**

### **3.5.1 Field Parameters**

The field parameters of the sampled groundwater of the alluvial aquifers along the Buffels River are all shown in Table 3.1. The sampled groundwater is saline, with the minimum EC values of 1.4mS/cm, 1.4mS/cm and 1.6mS/cm respectively for the three sampling seasons. These low EC values were recorded at BH01, BH02 and S12 samples, which are all situated above the mining activities along the river. The maximum EC values in all three sampling seasons were measured at S07, with EC values above 20mS/cm (which is the detection limit of the used EXTECH probe). High EC values were recorded during the dry seasons (March 2013 and February 2014) as compared to the wet season (September 2013). The pH values are mainly neutral, with an acidic groundwater sample with a pH of 4.8 measured at the hand dug well (W06) in March 2013. Low pH values of 5.1 and 5.4 were also measured at B09, the treated shaft water used at the Spektakel Mine in September 2013 and February 2014. There are large variations on the measured alkalinity ( $\text{HCO}_3$ ) of the groundwater,

ranging from 56-536 mg/L, 16-464 mg/L and 2-416mg/L respectively for the three sampling seasons. Low alkalinity was measured at B09.

### 3.5.2 Chloride Concentration

#### 3.5.2.1 Cl concentration in groundwater

The chloride concentrations in the groundwater samples range from 298-14588 mg/L, 278-12748 mg/L and 209-11217 mg/L respectively for the three sampling campaigns (Table 3.1). Chloride concentrations in groundwater were also high during dry seasons, as compared to the wet season. As with the EC, the highest chloride concentrations were measured at S07. The lowest EC values were measured at S12, B01 and B09 respectively.

#### 3.5.2.2 Cl concentration in precipitation

The measured amounts of precipitation in the region for 2013 and 2014 are tabulated in Table 3.3, with their analysed chloride concentration as well as  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopic compositions. The chloride concentrations in rainwater range from 0.7-22 mg/L with an average weighted chloride of 5.9 mg/L (Table 3.5). The maximum chloride concentration in rainwater was measured at Kleinzee near the coast. Most of the bromide concentrations were below the detection limit of 0.05 mg/l, with two rainwater samples measuring bromide concentrations of 0.4 and 4.4mg/L respectively. There are significant variations on the chloride concentrations of the rainwater with distance from the coast as well as on different raining dates, but no correlation was found between the precipitation amount and the chlorine concentration of rainwater (Fig. 3.3).

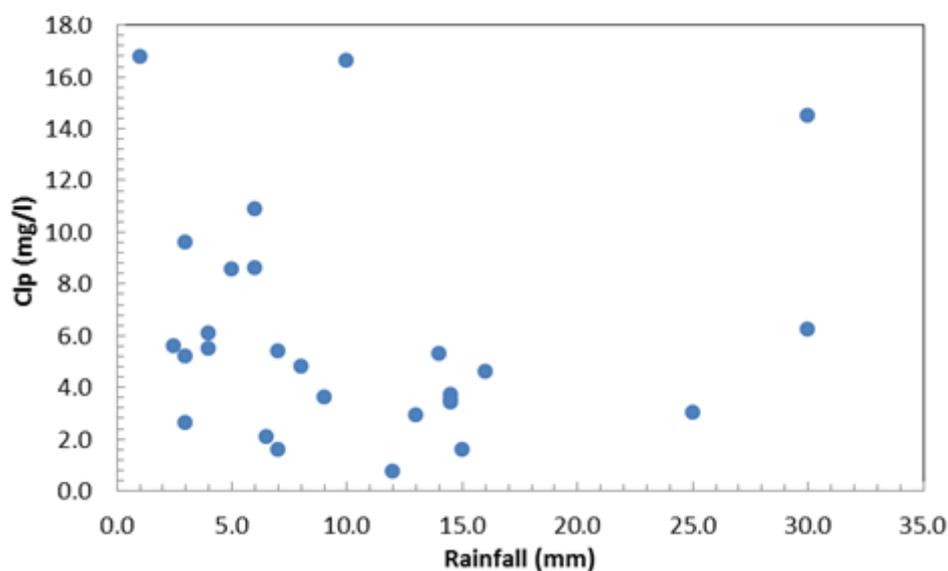


Figure 3.3: Chlorine in precipitation and rainfall amount correlation

### 3.5.3 Stable Isotopes

#### 3.5.3.1 $^{18}\text{O}$ and $^2\text{H}$ in groundwater

The stable isotopic composition of  $^{18}\text{O}$  and  $^2\text{H}$  of the groundwater samples for the three sampling campaigns are shown in Table 3.2, and plotted in the  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  diagrams (Fig. 3.4). The  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  diagrams are plotted together with the global meteoric water line (GMWL) of Craig (1961) and the local meteoric water line (LMWL). The  $\delta^2\text{H}$  values in groundwater range from -18.2 to -0.13‰, -16.1 to -1.9‰ and -17.8 to -0.9‰ respectively for the three sampling seasons. Moreover,  $\delta^{18}\text{O}$  values range from -3.82 to -0.13‰, -3.70 to 0.14‰ and -3.40 to 0.99‰ respectively. The stable isotopes in the groundwater show no significant changes between the dry and wet season's isotopes.

Deuterium excess in groundwater ranged from -4.58 to 13.36‰, -3.02 to 15.13‰ and -8.84 to 11.53‰ respectively for the three sampling seasons (Table 3.2). Sample S07 is the only sample with negative deuterium excess compositions in all the sampling seasons.

#### 3.5.3.2 $^{18}\text{O}$ and $^2\text{H}$ in precipitation

The  $\delta^2\text{H}$  values in the rainwater range from -45.9‰ to 13.4‰, while  $\delta^{18}\text{O}$  values range from -7.32 to -0.97‰. The heavy isotopes are generally increasing with late winter rains, having early rains enriched on light isotopes. The stable isotopes of rainwater samples were used to determine if the isotopic composition of the rainfall is similar or different from the Global Meteoric Water Line (GMWL) of Craig (1961). The Local Meteoric Water Line for this study area was determined by rainwater samples taken from the Naries Guesthouse, Komaggas and Kleinzee. The data is shown in Table 4. The LMWL is defined by the following equation:

$$\delta^2\text{H} = 7.7\delta^{18}\text{O} + 19.3 \quad \text{Equation 6}$$

Table 3-1: Tabulated field parameters and chloride concentrations of the groundwater

	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
<b>Location</b>												
Latitude	29°44.927'	29°44.171'	29°41.481'	29°39.209'	29°38.777'	29°35.074'	29°34.286'	29°39.697'	29°39.469'	29°38.144'	29°38.233'	29°59.523'
Longitude	017°38.199'	017°37.686'	017°35.683'	017°04.651'	017°05.826'	017°14.492'	017°18.176'	017°34.887'	017°34.867'	017°32.281'	017°32.304'	017°52.473'
<b>EC (mS/cm)</b>												
Mar-2013	1.4	1.5	3.2	3.8	2.6	4.8	20.0	12.9	6.1	4.7	2.9	1.4
Sep-2013	1.4	1.4	2.8	3.8	3.6	4.8	20.0	12.4	7.8			2.2
Feb-2014	1.7	1.6	3.1	4.0	4.2		20.0	12.8	8.8	6.7		
<b>pH</b>												
Mar-2013	7.3	7.2	6.8	7.0	6.6	4.8	7.3	7.2	7.5	7.2	7.5	7.6
Sep-2013	7.3	7.4	6.9	7.3	7.0	7.3	7.6	7.4	5.1			7.5
Feb-2014	7.3	7.5	6.6	6.7	6.9		7.0	6.8	5.4	7.2		
<b>Temp (°C)</b>												
Mar-2013	24.0	24.2	28.4	26.3	26.3	25.6	25.9	27.2	28.3	28.7	29.5	19.8
Sep-2013	22.4	22.4	20.4	18.2	16.6	22.2	21.5	22.9	23.0			12.8
Feb-2014	27.8	29.1	32.0	22.1	29.8		31.7	28.9	31.8	32.0		
<b>HCO<sub>3</sub> (mg/L)</b>												
Mar-2013	87.6	536.0	116.0	164.0	84.0	56.0	228.0	310.0	120.0	128.0	118.0	528.0
Sep-2013	78	118	142	154	232	108	464	430	16			162
Feb-2014	120	80	140	216	190		296	416	2	114		
<b>Cl (mg/L)</b>												
Mar-2013	325	320	930	1229	725	1854	14588	5944	2657	1472	763	298
Sep-2013	278	281	774	1123	1030	1606	12748	4612	2459			466
Feb-2014		231	273	812	1098	1169		11217	2484	209	746	

Table 3-2: Stable isotopes and deuterium excess of the groundwater

	B01	B02	B03	B04	S05	W06	S07	B08	B09	W10	W11	S12
<b>δ<sup>2</sup>H (‰)</b>												
Mar-2013	-15.0	-12.3	-7.2	-6.3	-7.8	-7.3	-5.6	-12.7	-8.7	-11.4	-10.6	-18.2
Sep-2013	-14.5	-14.0	-5.2	-8.8	-8.8	-6.6	-1.9	-16.1	-6.9			
Feb-2014	-17.8	-13.8	-5.9	-9.3	-9.2		-0.9	-15.8	-8.5	-7.8		
<b>δ<sup>18</sup>O (‰)</b>												
Mar-2013	-3.23	-2.81	-1.84	-1.83	-2.64	-1.98	-0.13	-2.94	-2.07	-2.68	-2.84	-3.82
Sep-2013	-3.70	-3.23	-2.09	-2.39	-2.43	-2.08	0.14	-3.29	-1.85			
Feb-2014	-3.33	-3.16	-1.93	-2.45	-2.52		0.99	-3.40	-2.32	-2.42		
<b>Deuterium Excess (‰)</b>												
Mar-2013	10.84	10.18	7.49	8.31	13.36	8.53	-4.58	10.83	7.89	10	12.13	12.41
Sep-2013	15.13	11.78	11.51	10.26	10.66	10.08	-3.02	10.19	7.94			
Feb-2014	8.84	11.46	9.5	10.26	10.95	0	-8.84	11.38	10.06	11.53		

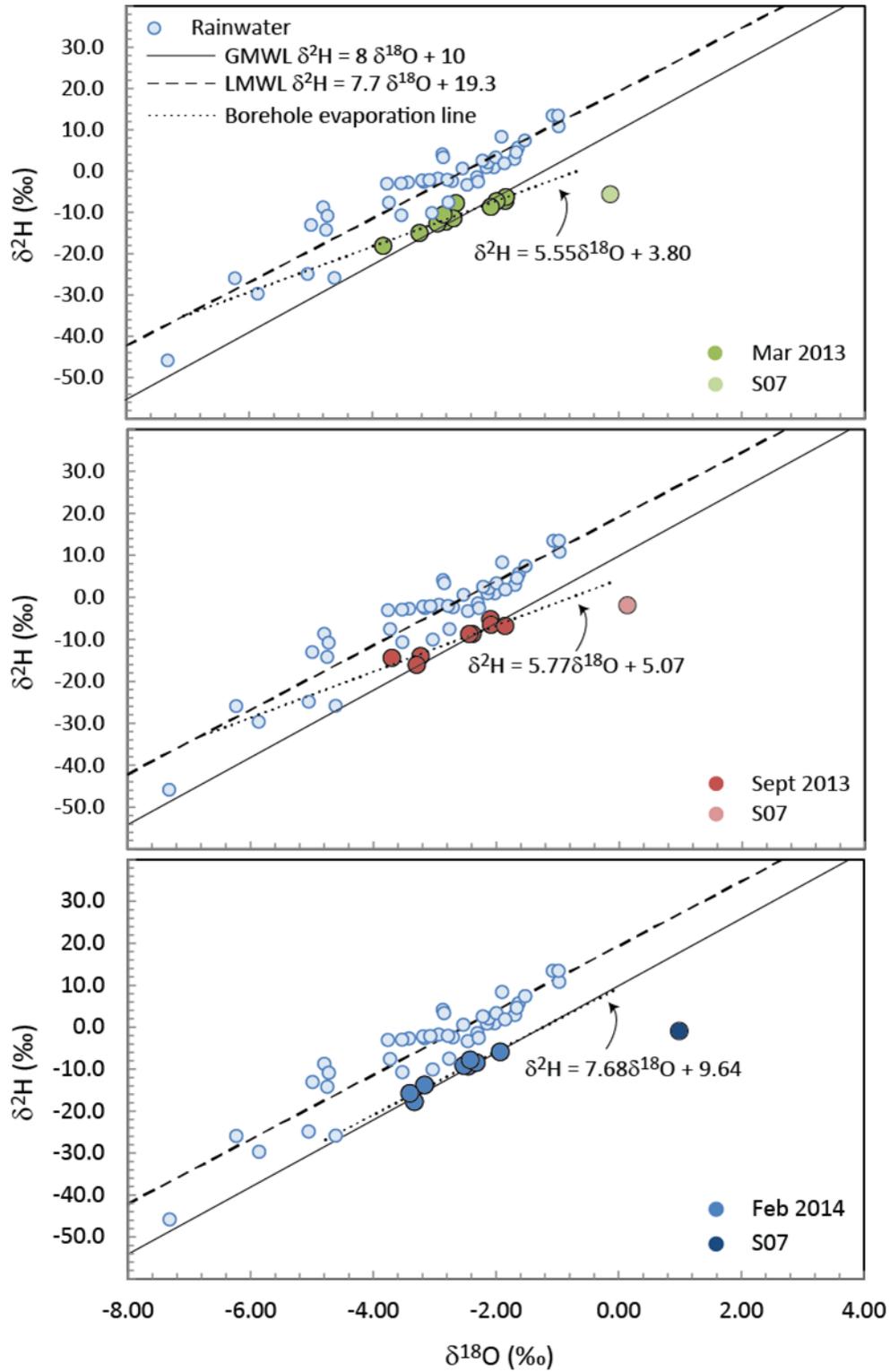


Figure 3.4: The stable isotope plots of the groundwater samples with respect to the LMWL and GMWL

Table 3-3: Stable isotopes and chloride concentration of rainwater

	Rain					
	Date	(mm)	Cl (mg/L)	Br (mg/L)	$\delta^2\text{H}(\text{‰})$	$\delta^{18}\text{O}(\text{‰})$
<b>Naries</b>						
<b>Guesthouse</b>						
	30.03.201					
	3	15.0			-45.9	-7.32
	31.03.201					
	3	15.0			-29.7	-5.86
	01.04.201					
	3	8.5			-7.6	-2.76
	17.04.201					
	3	2.0			2.9	-1.69
	18.04.201					
	3	19.5			-10.1	-3.03
	01.06.201					
	3	13.0	2.9		-14.2	-4.75
	02.06.201					
	3	8.0	4.8		-7.6	-3.73
	03.06.201					
	3	6.0	8.6		-8.7	-4.80
	12.06.201					
	3	14.5	3.7		-2.6	-3.16
	25.06.201					
	3	14.0	5.3	0.4	5.6	-1.63
	02.07.201					
	3	16.0	4.6		-3.1	-3.76
	15.07.201					
	3	3.0	5.2		0.9	-2.02
	18.07.201					
	3	7.0	5.4		-3.3	-2.46
	07.08.201					
	3	3.0	9.6		-1.4	-2.30
	10.08.201					
	3	14.5	3.4		-2.7	-3.42
	11.08.201					
	3	14.5	3.5		-3.0	-3.53
	12.08.201					
	3	4.0	6.1		-10.7	-3.52

	3				
	13.08.201				
	3	15.0	1.6	-1.8	-2.93
	14.08.201				
	3	2.5	5.6	0.6	-2.53
	15.08.201				
	3	3.0	2.6	0.9	-2.14
	16.08.201				
	3	7.0	1.6	2.1	-2.12
	17.08.201				
	3	6.5	2.1	3.3	-1.99
	29.08.201				
	3	25.0	3	-24.9	-5.05
	30.08.201				
	3	9.0	3.6	4.4	-10.9
	24.03.201				
	4	6.0	10.9	-2.4	-2.70
	25.03.201				
	4	12.0	0.7	-26.0	-6.23
	02.04.201				
	4	30.0	14.5	-2.2	-3.19
	09.05.201				
	4	10.0	16.7	4.1	-2.86
	29.05.201				
	4	4.0	5.5	-2.6	-2.28
	01.06.201				
	4	5.0	8.6		
	04.06.201				
	4	30.0	6.3	3.3	-2.85
	05.06.201				
	4	1.0	16.8		
<b>Kleinzee</b>					
	16.08.201				
	3	4.0	22	12.1	-0.67
<b>Komaggas</b>					
	28.08.201				
	3	27.5		-25.9	-4.61
	30.08.201				
	3	14.5		-13.1	-4.99

06.08.201	3	2.9	-2.1	-2.78
17.08.201	3	4.1	8.3	-1.90
13.08.201	3	7.1	10.8	-0.97
11.08.201	3	5.5	7.4	-1.52
17.07.201	3	4.0	4.6	-1.66
15.08.201	3	3.1	13.4	-1.07
29.08.201	3	10.0	-2.1	-3.07
14.08.201	3	1.0	13.4	-0.98
13.07.201	3	1.4	2.5	-2.21
18.07.201	3	1.1	1.8	-1.85

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#### **3.5.4 Estimated Recharge**

The recharge rates calculated using the CMB method are very low and ranges from 0.1-3.4 mm/a, with the highest recharge rates measured at BH01 (Buffelsrivier communal borehole) and the lowest measured at S07 (Table 3.5). This is only 0.1-2.1% of the annual precipitation in the region. Higher recharge rates in the range of 1-10% of the annual precipitation were estimated using the simulation method at 5mg/l and 20mg/l chloride concentration in rainfall (Fig. 3.5). Recharge rates are higher when rainwater has high chloride concentration (20mg/l). Rainfall with chloride concentration of 5mg/l only recharges 1% of the annual precipitation to yield the chloride concentration range in the groundwater (shaded area in Fig. 3.4).

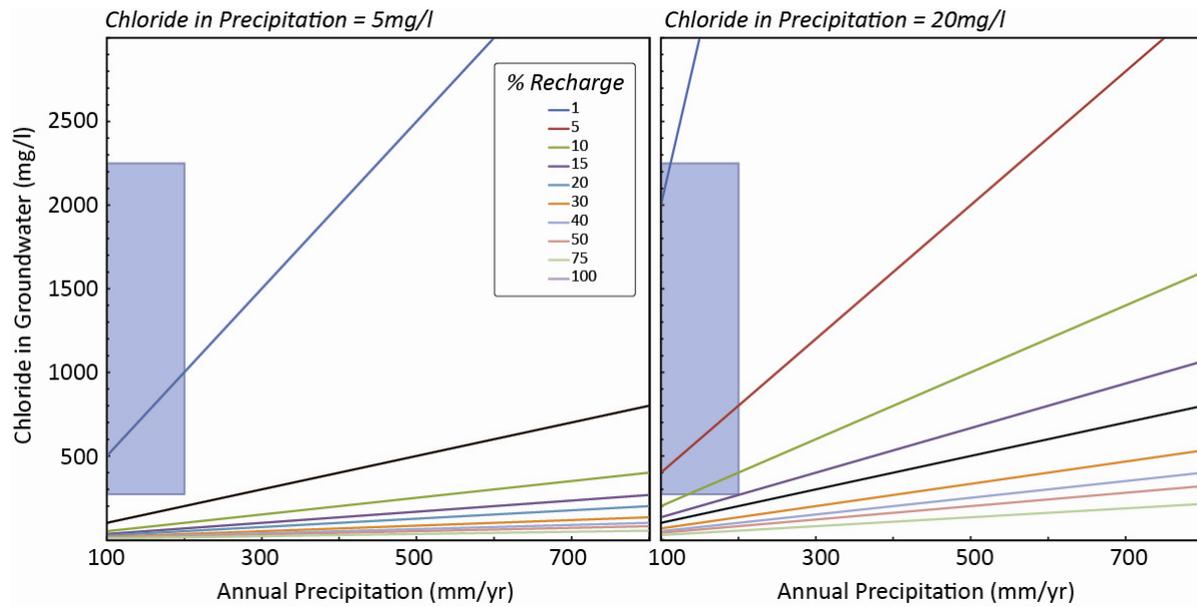


Figure 3.5: Simulated recharge indicated as percentages of the annual precipitation

Table 3-4: Summary statistics of the chloride concentrations in the rainwater samples taken at Naries Guesthouse

Statistics	Cl (mg/l)
Mean	6.7
Standard Deviation	4.4
Minimum	0.7
Maximum	16.8
Weighted average	5.9

Table 3-5: The calculated recharge rates using the CMB method

Site	Borehole	Annual rainfall	Average CI in rainfall	CI in groundwater	Recharge
		(mm/a)	(mg/l)	(mg/l)	(mm/a)
Buffelsrivier	B01	157.9	5.9	277.9	3.4
Buffelsrivier	B02	157.9	5.9	291.4	3.2
Buffelsrivier	B03	157.9	5.9	838.6	1.1
Kleinzee	B04	88.5	19.1	1149.8	1.5
Kleinzee	S05	88.5	19.1	974.5	1.7
Near Kleinzee	S07	88.5	19.1	12850.9	0.1
Buffelsrivier	B08	157.9	5.9	4346.6	0.2
Buffelsrivier	B09	157.9	5.9	1775.1	0.5
Near	W10	157.9	5.9	1109.0	0.8
Buffelsrivier					
Near	W11	157.9	5.9	763.0	1.2
Buffelsrivier					
At N7	S12	217.1	2.42	382.0	1.4

### 3.6 Discussion

#### 3.6.1 Recharge Mechanisms

Recharge to the alluvial aquifers along the Buffels River is derived from rainwater and floodwater infiltration (Benito et al., 2010). Stable isotopes are used in recharge studies to examine sources of water, flow patterns as well as the mixing processes in the groundwater flow system of the area (Clarke and Fritz, 1997). In this study, stable isotopes of groundwater were used to determine whether recharge was direct or delayed. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes indicate that recharge to the groundwater is delayed; indicated by fractionated groundwater stable isotopes in relation to the LMWL (Fig. 4, 5 and 6). This is indicating that most of the groundwater has undergone some degree of evaporation prior or during infiltration. Evaporation results on the concentration of dissolved constituents in water and the enrichment of the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes. Recharge from lateral flows is reportedly dominant for the Buffels River alluvial aquifers (Watchtler 2006).

The groundwater samples plot on the GMWL which has a shallower gradient than the LMWL (Fig. 4, 5 and 6). This indicates the deuterium excess effects, predominant in the coastal regions of the northern hemisphere. Studies in Central Namaqualand by Adams et al., (2004) also show shallower GMWL gradients to the LMWL. The deuterium excess values for all the groundwater samples are positive, except at S07. The positive deuterium excess indicate modern water and low degrees of

evaporation (Murad, 2014) while negative deuterium excess indicates greater degrees of evaporation and/or old recharge.

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopes are used to trace the mechanisms that have altered the isotopic composition of the recharging precipitation to the current composition of the sampled groundwater in the area (Adams et al., 2004). Rainwater in the study area shows a wide range of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values reflecting the extent of isotopic fractionation during successive cycles of evaporation and condensation of water originally evaporated from the sea. The isotopic signatures of the groundwater in the study area also confirm to the modification of the recharging precipitation. This is caused by the evaporation effects either before or during infiltration of groundwater as well as by the leaching of previously evaporated salts on the ground surface and in the unsaturated zone (Adams et al., 2004).

A weak correlation was found between the precipitation amount and the chlorine concentration of rainwater for the individual samples (Fig. 3). A similar trend of a weak correlation between rainfall and the chloride concentration in rainwater was reported in groundwater by Adams et al., (2004). However, the chloride concentration in the rainwater decreases with increasing rainfall. This is because with low rainfall, the aerosol particles are not diluted but are concentrated in the rainfall occurring in a particular area.

### **3.6.2 The Recharge Rates from Chloride Mass Balance**

The recharge rates calculated using the CMB method are in the ranges of 0.1-3.4mm/a. However, the CMB method assumes all the chloride in the groundwater is of atmospheric origin. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the groundwater from the alluvial aquifers along the Buffels River indicate there is additional chloride to the groundwater from the dissolution of rock mass (Chapter 2). The additional chloride from the geological unit results in underestimated recharge rates. To account for the additional chloride concentration, a simulation model was run to determine the percentages of precipitation that is recharged to yield the measured chloride concentrations in the groundwater. The simulation indicates that high chloride concentrations are measured in the groundwater when the recharge amounts are low (0.1-5% of annual precipitation). This is in agreement with the recharge rates measured with CMB method, where samples with high chloride concentrations i.e. S07 measured the lowest recharge rates. The higher recharge rates were measured at B01 and this recorded the lowest chloride concentration as well.

The region also experiences different precipitation amounts at different areas, and recharge rates are therefore different for the different areas along the Buffels River. Low recharge rates were measured in the groundwater samples near the coast. The low recharge rates for the coastal aquifers can be attributed to the low precipitation amount in the area. Furthermore, higher recharge rates (3.4mm/a and 3.2mm/a) were measured in groundwater samples with low chloride concentrations (B01 and B02) as compared to those with high chloride concentrations (S07 and B08). This can be attributed to

high evaporation rates, which minimises the water available for recharge and concentrates the chloride concentration in the residue water.

The differences in recharge rates to these alluvial aquifers are also related to the nature of the aquifers (Adams et al., 2004). The aquifers' soil properties have an effect on the recharge rates, with clay soils having low recharge rates as compared to sand soils. In the Buffels River, the alluvial aquifers are mostly sandy. When the rain is above average, the river flows and the runoff carries the mud and clays with. These are mostly accumulated in depressions where the runoff water stands. The recharge rates are therefore low in aquifers with clay than the sandy aquifers. A thin clay layer was found at S05 in February 2014 and this can have an impact on the recharge resulting in the measured low rates at the site.

### **3.7 Conclusion**

Recharge to the alluvial aquifers is from the infiltration of rainwater. The stable isotopes of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in groundwater show fractionated isotopes in comparison to the stable isotopes in the rainwater. This indicates that the recharge to the alluvial aquifers is delayed, and the groundwater is evaporated prior or during infiltration. The recharge rates to the alluvial aquifers along the Buffels River estimated using the CMB method are low, and ranges from 0.1-3.4mm/a. The maximum recharge rates (3.4mm/a) were measured in groundwater at Buffelsrivier and the lowest were measured near Kleinzee at the coast. The CMB method assumes the chloride concentration in the groundwater is all of atmospheric origin (both dry and deposition). However, the groundwater samples have additional chloride from the dissolution of the rock mass. The additional chloride concentration removes the mass balance between chloride in recharge and in groundwater. The additional chloride has an impact on the calculated recharge rates, as it underestimate the recharge rates. This was verified by running a simulation model which indicates that recharge rates are in the ranges of 1-5% of the total precipitation in contrast to 0.1-2.1% estimated by the CMB method. However, the recharge rates to the alluvial aquifers are generally low, and recharge rate estimates from the CMB method are still significant but just not accurate and need to be supported by estimates from other estimating methods.

#### Chapter 4: **General Conclusion and Recommendations**

Groundwater salinity is a major problem in the groundwater resources of Namaqualand, with the shallow alluvial aquifers along the Buffels River where this study was done also having high salt-loads. The chemical and isotopic studies of the groundwater indicate that there are multiple salt sources to these aquifers. Most of the salts are mainly derived from the dissolution of rock mass, as well as concentrated by evapotranspiration processes. Identifying the salinity sources to these alluvial aquifers is critical for they are the main water source to the communal communities both for domestic and agricultural purposes. The groundwater is also used in the copper and diamond mining activities along the river. However, high salinities were measured in boreholes close to the mining activities along the river. Future studies can therefore look into the effects of the mining activities on the groundwater chemistry of these shallow alluvial aquifers.

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  stable isotopes of the groundwater indicate the recharge to the alluvial aquifers is indirect, and groundwater shows an evaporative trend with respect to the LMWL. Groundwater is therefore evaporated prior or during infiltration. The high evaporation rates cause the enrichment of heavy  $^{18}\text{O}$  and  $^2\text{H}$  stable isotopes in the groundwater and concentrate the dissolved ions causing high salt-loads in the groundwater system. Evaporation rates in Namaqualand have been estimated in an earlier study by Adams et al., (2004) but quantification of the total evaporation from the shallow groundwater has not been done. As the groundwater in the alluvial aquifers is very shallow (the deepest at 7m), direct evaporation from the groundwater is possible. Recommendations are therefore made in this study to look into how much evaporation has the groundwater been exposed to.

The CMB method used in the estimation of recharge rates assumes all the chloride concentrations in the groundwater are of atmospheric origin (both dry and wet depositions). For the alluvial aquifers along the Buffels River, there is additional chloride from the dissolution of rock mass. The non-atmospheric chloride removes the balance between chloride in precipitation and in the groundwater. The recharge rates based on the CMB method are low, in the range of 0.1-3.4mm/a (0.1-2.1% of the annual rainfall). Higher recharge rates in the range of 1-5% of the annual precipitation were determined from a simulation model run to detect the percentages of annual precipitation that are recharged to the groundwater, to get the current chloride concentrations measured in groundwater. The direct usage of the CMB method therefore underestimates the estimated recharge rates to the alluvial aquifers. However, the CMB method still gives significant recharge rates, but inaccurate and needs to be supported by another recharge estimating method. Thus, future studies can apply other arid and semi-arid suitable recharge estimation methods (i.e. GIS models) and compare the recharge rates to the ones produced in this study using the CMB method.

Moreover, the chloride concentrations in the granitic and gneiss rock masses of the Buffels River have not been quantified. It is therefore not certain how much of the salts in the groundwater are derived from the dissolution of rock mass. Future studies can look into determining the chloride and sodium concentrations in the granites and gneisses in the region. In addition to the chloride from rock mass

dissolution, the dry chloride deposition in the region was assumed to be negligible. However the lower catchment is on the coastal region and dry deposition from the Atlantic Ocean can be significant. Future studies can also look into quantifying the deposition of dry chloride in Namaqualand.

The salinity sources to the alluvial aquifers are natural, with the exemption of the salts from the mining activities. It is therefore difficult, if not impossible to mitigate. The natural sources are regional, and this explains the saline groundwater chemistry of the Namaqualand region. However, salinity from the mining activities can be remediated through proper handling of the mine wastes. Groundwater can be treated through the desalinisation process to make it suitable for the intended uses. However, desalination is expensive especially on a large scale.

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