Isotopic and elemental ratios to assess the relationship between heuweltjies and saline groundwater in the Northern Cape of South Africa.

Jani van Gend

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Department of Earth Science, Stellenbosch University

Supervisor: Prof Jodie Miller

Co-Supervisors: Dr. Catherine Clarke and Dr. Michele Francis

Declaration

I hereby declare that the entirety of the work contained herein is my own, original work, that I am the authorship owner thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification. This thesis is submitted in fulfilment of a Doctor of philosophy in the department of Earth Science, Stellenbosch University.

Full name: Jani van Gend

Signature: ______________________________

Signed on: ______________________________

Abstract

Globally, groundwater is becoming one of the most important resources. This is specifically the case in semi-arid to arid southern Africa where surface water resources are limited. In the Buffels River catchment, part of a coastal desert and global diversity hotspot in Namaqualand, South Africa, many communities and the local economy are largely dependent on groundwater as the only source of potable water in the region. However, the groundwater is variably saline. In this study, hydrochemistry and stable and radiogenic isotopes from groundwater in the Buffels River catchment is used to determine the origin of salts in the groundwater as well as the mechanism of salinisation. In order to do this, a better understanding of the aquifer systems was required. Basic cation and anion data together with $\delta^{18}O$, $\delta^{2}H$ and $^{87}Sr/^{86}Sr$ data indicated that evaporative concentration of salts is not the main contributor to salinisation as previously thought, but that dry deposition of marine aerosols and water-rock interaction are the main sources of salts. Heuweltjies are prominent features in this region and it was known that they generally consist of nutrient rich soils, but geophysics data revealed that these soils are extremely saline with the salinity increasing with depth and towards the centre of the heuweltjie. Thus, heuweltjies are zones where salts accumulate and given that heuweltjies consist of aerated soils and contain tunnels which could act as preferential flow paths, their contribution to salinisation was further investigated. A new groundwater recharge model for was conceptualised which include recharge through heuweltjies, and total mean groundwater ages were calculated using a combination of ^{14}C and ^{3}H and a lumped parameter approach to understand when recharge has been taking place. The age of groundwater in the Buffels River catchment range between modern and ~18 000 years, with modern fraction of up to 80 %. The relationship between heuweltjie salts and saline groundwater was further investigated by determining the relative depths and ages of the different carbonate horizons. Heuweltjies are up to ~30 000 years old and three distinct wetting fronts, which is an indication of mean annual rainfall amounts, are seen. This proved that heuweltjies act as preferential flow paths and that salts are transported downwards through the centre of the heuweltjies. $\delta^{18}O$ SO_4^{2-} and $\delta^{34}S$ SO_4^{2-} isotope signatures of heuweltjie soils indicated that the salts in heuweltjies is directly related to dry deposition of aerosols containing both marine and non-marine-salts. $\delta^{18}O$ SO_4^{2-} signatures of groundwater hosted in the granitic gneisses are similar to that of the heuweltjies, suggesting that the mechanism of formation of these salts are the same, while the $\delta^{34}S$ SO_4^{2-} signature indicate a “granitic gneiss”-influence. In contrast to this. In areas were the heuweltjie density is high, the $\delta^{34}S$ $SO_4^{2-}$and $\delta^{18}O$ SO_4^{2-} signatures of groundwater and heuweltjie soils are comparable indicating that salts stored in heuweltjies are flushed into the aquifer system and that heuweltjies play a role in salinisation of groundwater and have been doing so for thousands of years.

List of Publications

Peer Reviewed Journals

van Gend, J., Francis, M.L., Watson, A.P., Palcsu, L., Horváth, A., Macey, P.H., le Roux, P., Clarke, C.E. and Miller, J.A., 2020. Saline groundwater in the Buffels River catchment, Namaqualand, South Africa: A new look at an old problem. Science of The Total Environment, p.143140. Impact factor: 6.551

Book section:

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CHAPTER 1.

Introduction

1.1. General Introduction

Freshwater scarcity has been a major global concern for decades and is one of the main inhibitors to global economic development and food security (Döll, 2009; Veldkamp, Wada, Aerts, *et al.*, 2017; Vörösmarty, Green, Salisbury, *et al.*, 2000; Vörösmarty, McIntyre, Gessner, *et al.*, 2010; Wada, Van Beek, Van Kempen, *et al.*, 2010; Wheeler & von Braun, 2013). Where the focus used to be on fresh surface water, in recent years it has shifted to groundwater as one of the major sources of fresh water in many parts of the world and groundwater resources are becoming increasingly vulnerable in terms of both quality and quantity (Döll, Hoffmann-Dobrev, Portmann, *et al.*, 2012; Huggins, Gleeson, Kummu, *et al.*, 2020; van Rooyen, Watson & Miller, 2020; Wada & Bierkens, 2014). This increase in groundwater use is specifically seen in semi-arid to arid environments where groundwater resources are often non-renewable (Bierkens & Wada, 2019; Jasechko, Perrone, Befus, *et al.*, 2017; Scanlon, Keese, Flint, *et al.*, 2006; Wada, Flörke, Hanasaki, *et al.*, 2016). Many of these semi-arid to arid regions are located in developing countries, such as India, Pakistan and many countries in Africa, where the population density is high and pressure on resources, especially potable water, is already a major challenge (Döring, 2020; Huggins *et al.*, 2020; Igor S. Zektser, 2004). To add to this, the global population is expected to increase to 9.7 billion people by 2050 with much of this increase occurring in sub-Saharan Africa (UNDESA, 2019). In this region the population is expected to grow by over one billion additional people by 2050 (UNDESA, 2019) which will increase the pressure on the groundwater resources even more. Moreover, with an increase in population comes a rapid increase in urbanisation to cities, rapid urban development, growing food demands, expansion of irrigated land and a substantial increase in the dependence on groundwater in regions where groundwater is already vulnerable to exploitation (Adelana, Abiye, Nkhuwa, *et al.*, 2008; Lapworth, Nkhuwa, Okotto-Okotto, *et al.*, 2017; Schmidhuber & Tubiello, 2007; Sheffield, Wood, Chaney, *et al.*, 2014).

In addition to increasing demand for natural resources as a result of the growing population, climate change will also have an effect on the availability and quality of fresh water. This is specifically the case in Sub-Saharan Africa, one of the regions predicted to suffer most from the impacts of climate change (Connolly-Boutin & Smit, 2016; WWAP - UNESCO World Water Assessment Programme, 2019). This is due to several reasons, including: (1) the region's dependence on agriculture and natural resources (Fjelde & von Uexkull, 2012; Thornton, Jones, Owiyo, *et al.*, 2008); (2) the lack of information about and the slow technological development in sub-Saharan Africa (Kotir, 2011); (3) the communities' low capacity to adapt (Pereira, 2017; Thomas & Twyman, 2005); (4) and increasing variability in rainfall in this region causing increasing frequency of droughts and flooding (WWAP, 2019;

Thornton et al., 2015; UNESCO, 2020). Given that agriculture is one of the largest economic contributors in this region, with the livelihoods of 70% of the population in sub-Saharan Africa depending on agriculture (Connolly-Boutin & Smit, 2016; Sheffield *et al.*, 2014), the availability of water is one of the limiting factors in terms of economic development. Up until recently, the agricultural sector in this region has mainly relied on rainfall and surface water resources for irrigation purposes (Villholth, 2013; WWAP, 2019; Döring, 2020). However with increasing temperatures and changing rainfall patterns caused by climate change, these resources are not sustainable, resulting in the use of alternative water sources, more specifically groundwater (Cobbing & Hiller, 2019).

Although much of sub-Saharan Africa is regarded as vulnerable to climate change, the effects are likely to be more pronounced in southern Africa (Nhamo, Ebrahim, Mabhaudhi, *et al.*, 2019; Vogel & Olivier, 2019). This is particularly evident along the west coast of South Africa and Namibia, where precipitation is already very low and surface water resources limited and the dependence on groundwater is increasing, with some communities already wholly dependent on groundwater as the only source of potable water. Recent climate change affecting the region, is changing the way in which precipitation is received, with fewer precipitation events with higher precipitation amounts being received resulting in a greater dependence on groundwater (Davis, Hoffman & Roberts, 2016). However, while the groundwater is moderately to severely saline the groundwater is not affected by the same degree of salinisation across the region. Salinisation of groundwater in semi-arid to arid regions is typically ascribed to evaporative concentration of salts on the surface after which these salts are transported downwards as brines during episodic rainfall events (Rengasamy, 2006; Schoups, Hopmans, Young, *et al.*, 2005; Vengosh, Spivack, Artzi, *et al.*, 1999; van Weert, Van Der Gun & Reckman, 2009; Wu, Li, Qian, *et al.*, 2014). This is also thought to be the case along the west-coast of southern Africa (Adams, Titus & Xu, 2004; Benito, Rohde, Seely, *et al.*, 2010). However, if this was the case, the spatial distribution of saline groundwater would be more uniform across the entire region experiencing the same climatic conditions. Most of the west coast of South Africa and a large part of the western inland receive similar MAP (Figure 1. 1a and b) and the potential evaporation along the west coast is high, but there are regions with higher potential evaporation and higher surface temperatures and yet, the electrical conductivity of the groundwater in these regions are not as elevated (Figure 1. 1 c and d adapted from van Rooyen, (2020)). This suggests that evaporative concentration of salts as a result of the climatic conditions, may not be the controlling factor in the salinisation process.

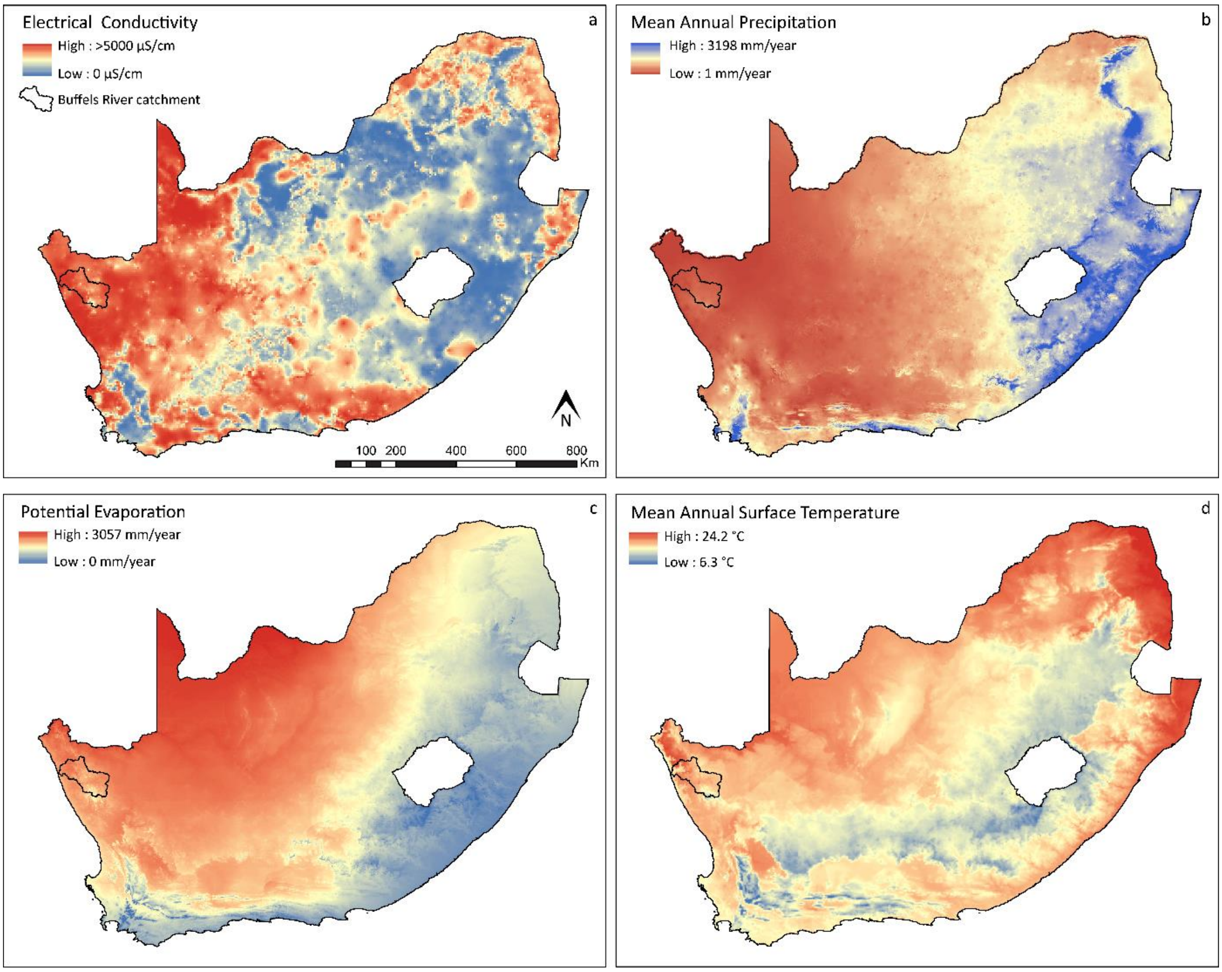

Figure 1. 1: Electrical conductivity variation in groundwater across South Africa compared to the climatic conditions in the same area, specifically indicating the variability in groundwater EC along the west coast of South Africa. a) Electrical conductivity variation in groundwater; b) Mean annual precipitation across South Africa; c) Variation in potential evaporation; d) Mean annual surface temperature. Adapted from van Rooyen, (2020).

One of the notable biophysical features of the landscape along the west coast of South Africa, and specifically in the Namaqualand, a coastal desert in the Northern Cape of South Africa, are heuweltjies (little hills). These large lenticular mounds consist of aerated and nutrient-rich soils, containing elevated levels of micro and macro elements compared to the surrounding area known as the interheuweltjie (Kunz, Hoffman & Weber, 2012; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Midgley & Musil, 1990; Midgley, Harris, Harington, *et al.*, 2012a). They are typically up to three meters high and up to 60 m in diameter. There is some controversy around the origin and formation of heuweltjies but most authors agree that heuweltjies formed as a result of both paleo and modern termite activity, more specifically, the Southern Harvester termite (Microhodotermes *viator*) (McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; Midgley *et al.*, 2012a; Moore & Picker, 1991a; Picker, Hoffman & Leverton, 2007). As a result, heuweltjie soils are heavily bioturbated and large tunnels of up to a few centimetres in diameter exist within the heuweltjies. Given that heuweltjies consist of aerated soils and host these large tunnels and occupy between 14 and 25% of the landscape (Lovegrove & Siegfried, 1986; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; Picker *et al.*, 2007) they could play a role in contributing to groundwater recharge by acting as preferential flow paths, facilitating downwards water movement. If this is the case, heuweltjies would play a role in controlling the chemistry of the groundwater as the salts present in the heuweltjies may be flushed into the groundwater system. Moreover, heuweltjie carbonates have been determined to be more than 30 000 years old (Potts, Midgley & Harris, 2009), suggesting that heuweltjies may have contributed to salinisation of groundwater for thousands of years.

The Buffels River catchment is the largest catchment in Namaqualand, comprising an area of approximately 9250 km^2. Here, no surface water resources exist, and many communities are wholly dependent on groundwater. However, some boreholes have started to dry up, while the groundwater from many boreholes in use is variably saline. One of the main economic sectors in this region is agriculture in the form live-stock farming and although the live-stock were able to feed off the natural vegetation in the past, current periods of droughts has forced farmers to start cultivating pastures for additional feed which increased their dependence on groundwater (Cousins, Hoffman, Allsopp, *et al.*, 2007; Hoffman & Rohde, 2007). Apart from commercial agriculture, the livelihoods of many of the local communities, also rely on agriculture in the form of subsistence farming. Communal land has been allocated where herders roam with their livestock to graze, but they too rely on groundwater as the only source of water for their livestock. Therefore, further deterioration of groundwater quality through salinisation will be problematic not only for basic human consumption but for agricultural purposes (food security) and biodiversity in this semi-arid region.

This study will aid in better understanding the salinisation processes by specifically looking at the relationship between saline heuweltjie soils and saline groundwater in a semi-arid region where social and economic development is dependent on groundwater. Although the Buffels River catchment hosts most of the population of Namaqualand, large parts of the catchment have not been disturbed by anthropogenic activity, specifically the saline heuweltjie soils, which provides a unique opportunity to investigate the saline nature of both the soils and the groundwater. Knowledge of this relationship between heuweltjies and saline groundwater, will be able to assist in better groundwater management strategies and will aid in decision making for the future groundwater use in Namaqualand. Apart from the local implications of this study, heuweltjies also occur in the Western Cape of South Africa, in the region where most of the fruit and vegetables are produced in Southern Africa, for both exporting and local use. Here, heuweltjie soils have been cultivated and the effect that the heuweltjies may have on groundwater has not been established. By understanding groundwater movement through the heuweltjies and the salinisation process of groundwater, agricultural practices can be adapted to prevent deterioration of groundwater resources.

1.2. Problem Statement

It is known that heuweltjies consist of saline soils, but the relationship between saline heuweltjies soils and saline groundwater has not been assessed. A holistic overview of all the environmental factors that could potentially play a role in contributing to salts in the groundwater system, including heuweltjies, is therefore required. The first step in achieving this, is to gain a better understanding of the aquifer system or systems in the Buffels River catchment in terms of the spatial variation in the hydrochemistry of the groundwater. Once this has been achieved, the hydrochemical character of the groundwater together with groundwater isotope ratios can be used to determine the origin of salts in the groundwater system. Recharge pathways will have to be assessed and a model of flow paths will have to be conceptualised to determine the mechanisms of salt transport into the groundwater system.

In order to understand the timing and period of the salinisation period, groundwater residence times should be determined. The use of radiocarbon with a dilution factor should be evaluated in order to determine whether the residence times can be determined accurately using the standard decay equation. Previous studies suggested that both tritium and radiocarbon are present in the groundwater in the Buffels River catchment, and the use of a lumped parameter model to determine to residence times could also be considered. Once the groundwater residence time has been determined and there is an indication of how long salinisation may have been taking place for, the role of heuweltjies in this process should be assessed. Carbonate horizons in heuweltjies, south of Namaqualand, are known to be older than 30 000 years, but heuweltjies in the Buffels River catchment have not been dated. However, these ages should be determined to constrain the period of salinisation. Furthermore, the ages of carbonate horizons together with their depths provide valuable information about past climatic events and their timing which in turn will provide an indication of salt flushing events. This should be compared to the age and chemistry of the groundwater to establish whether there is a relationship between past climatic events seen in heuweltjies and salinisation of groundwater. Lasty, by determining the sulphur isotope signature of heuweltjie soils and comparing it to that of the groundwater, it can be established whether heuweltjie salts contribute to the salinisation of groundwater.

1.3. Aims and Objectives

A number of aims and key questions were identified to assess and understand the relationship between groundwater chemistry, groundwater recharge, heuweltjies and climate change in the Buffels River catchment.

Aim 1: To characterise the groundwater in the Buffels River catchment in terms of hydrochemistry to better understand the cause of salinisation of groundwater in the catchment.

1.1. What is the spatial distribution of saline groundwater in the Buffels river Catchment, especially with respect to different aquifer types?

1.2. What is the hydrochemistry of the groundwater in the catchment in terms of major cations and anions along with $\delta^{18}O$, $\delta^{2}H$ values and $^{87}Sr/^{86}Sr$ ratios?

1.3. Where do the salts in the groundwater originate from?

1.4. What is the leading cause or causes of groundwater salinisation in the region and what is the role of heuweltjies in the salinisation process?

Aim 2: To understand the temporal relationships between groundwater in different areas of the catchment

2.1. How does the groundwater recharge occur and are the possible mechanisms in different regions of the catchment?

2.2. What information does the $\delta^{13}C_{DIC}$ values in groundwater in the catchment provide about ^{14}C dilution and what are the possible processes involved?

2.3. What is the age of the groundwater in the Buffels River catchment and how does this impact the sustainability of groundwater in the catchment?

2.4. Can the groundwater ages of the groundwater ages provide an indication of the period of salinisation?

Aim 3: To determine the mechanisms and timing of salt input in the groundwater of the Buffels River catchment

3.1. What is the age distribution of calcite in heuweltjies?

3.2. Is there a link between the salts in heuweltjies and saline groundwater?

3.3. How does the heuweltjie salts end up in the groundwater?

3.4. What is the relationship between the spatial distribution of heuweltjies and saline groundwater?
3.5. What does this relationship mean in terms of the future of groundwater use in semi-arid to arid environments where soils are affected by heuweltjies?

1.4. Thesis Layout

This thesis consists of three manuscripts. In the first manuscript titled "Saline groundwater in the Buffels River Catchment, Namaqualand, South Africa: A new look at an old problem", the hydrochemistry of the groundwater in the Buffels River catchment is outlined and the origin of the slats present in the groundwater is defined. This manuscript has been published in Science of the Total Environment journal. In the second contribution, "Impact of residence time constraints on groundwater sustainability and implications for agricultural development: A case study from the Buffels River catchment, Northern Cape, South Africa" recharge pathways are conceptualised and groundwater residence times are calculated to evaluate the sustainability of the resource. The third manuscript "Mechanisms and timing of groundwater salinisation in Buffels River catchment", further defines the conceptualised recharge pathways, evaluates the relationship between saline heuweltjie soils and saline groundwater, providing evidence of the origin of the salts present in the groundwater and details the mechanism and timing of groundwater salinisation in the Buffels River catchment. The second and third contributions will be submitted to peer reviewed journals after completion of the thesis.

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CHAPTER 2

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Saline groundwater in the Buffels River Catchment, Namaqualand, South Africa: A new look at an old problem.

J. van Gend[1], M.L. Francis[2], A.P. Watson[1], L. Palcsu[3], M. Molnár[3], P.H. Macey[4], P. le Roux[5], C.E. Clarke[2], J.A. Miller[1*]

1. Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, South Africa
2. Department of Soil Sciences, Stellenbosch University, Private Bag, X1, Matieland, South Africa
3. Isotope Climatology and Environmental Research Centre, Debrecen, Hungary
4. Council for Geoscience, PO Box 572, Bellville 7530, South Africa
5. Department of Geological Sciences, University of Cape Town, South Africa

* Corresponding Author: E-mail address: jmiller@sun.ac.za.

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Abstract

Namaqualand, South Africa, is a global biodiversity hotspot but local populations are affected by challenging economic conditions largely because of poor access to water. In this study groundwater types are characterised and sources of salts and salinisation processes are identified using hydrochemistry and $\delta^{18}O$, $\delta^{2}H$ and $^{87}Sr/^{86}Sr$ data. Analysis of $\delta^{18}O$ and $\delta^{2}H$ data suggests that evaporation does not play a major role in salinisation of the groundwater. However, major ion chemistry and $^{87}Sr/^{86}Sr$ ratios indicate that salts present in the groundwater are linked to dry deposition of marine aerosols and ion-exchange reactions in soils in the alluvial aquifer systems. The hydrochemical variability of the groundwater in the basement aquifer system suggests that there are strong local controls linked to weathering processes in individual basement rock types. The region is also notable for the high density of heuweltjies, biophysical features associated with increased nutrient levels, associated with termite activity. Electromagnetic scanning as well as measurement of water-soluble soil electrical conductivity values on and off heuweltjies, show that heuweltjies are saline with salinity increasing with depth. The level of groundwater salinity correlates with the level of heuweltjie salinity. Precipitation records from the last 150 years provide support for the hypothesis that accumulated salts, and in particular, heuweltjie salts are flushed into the groundwater system during sporadic large volume precipitation events. Thus, heuweltjies and hence termite activity, could potentially represent a previously unrecognized contributor to groundwater salinisation across Namaqualand and in other parts of the world.

2.1 Introduction

Salinisation of groundwater has been a global phenomenon for thousands of years across a range of climatic environments (Bouchaou, Michelot, Vengosh, *et al.*, 2008; Farber, Vengosh, Gavrieli, *et al.*, 2004; Karroum, Elgettafi, Elmandour, *et al.*, 2017; Petelet-Giraud, Négrel, Aunay, *et al.*, 2016; Vengosh, Gill, Davisson, *et al.*, in press). Natural processes that lead to groundwater salinisation include atmospheric deposition of windblown salts (Cruz-Fuentes, Cabrera, Heredia, *et al.*, 2014; Gamboa, Godfrey, Herrera, *et al.*, 2019), evaporation and evapotranspiration (Alvarez, Carol & Dapeña, 2015; Shanyengana, Seely & Sanderson, 2004), silicate and carbonate weathering (Chen, Ma, Du, *et al.*, 2014; Karroum *et al.*, 2017; Santoni, Huneau, Garel, *et al.*, 2016) and clay transformation (Hogan, Phillips, Mills, *et al.*, 2007; Meredith, Moriguti, Tomascak, *et al.*, 2013). Many of these processes are prevalent in semi-arid and arid environments and as a result these climates are particularly prone to salinisation of groundwater. Salinisation can also be driven by anthropogenic activities such as changes in land use (Foster & Chilton, 2003; Malki, Bouchaou, Hirich, *et al.*, 2017; Nosetto, Acosta, Jayawickreme, *et al.*, 2013), poor agricultural practices (Li, Wang & Xie, 2016; Tweed, Celle-Jeanton, Cabot, *et al.*, 2018), and over abstraction leading to ingress of seawater (Cardona, Carrillo-Rivera, Huizar-Alvarez, *et al.*, 2004; Mahlknecht, Merchán, Rosner, *et al.*, 2017; Werner, Bakker, Post, *et al.*, 2013). Where these processes occur in combination, they lead to a complex interplay of salinisation processes that makes the identification of the primary salinisation mechanism ambiguous. However, without identification of the primary salinisation mechanism, it is difficult to develop groundwater management strategies that would serve to mitigate the problem and facilitate economic development.

Namaqualand, on the west coast of southern Africa, is a semi-arid to arid coastal environment and one of only two desert regions world-wide recognised as a global biodiversity hot spot, in part because of the reliable nature of precipitation when compared to other arid regions worldwide with similar low mean annual precipitation (Desmet, 2007). The region has few freshwater resources and the Orange River is the only perennial river in an area of over 260 000 km^2 (Figure 2. 1a). The low mean annual precipitation combined with limited surface water resources means that the area is strongly dependent on groundwater to support human populations and economic activities. However, groundwater quality is extremely variable but generally substantially poorer than most other parts of South Africa. The saline-nature of groundwater has typically been ascribed to evaporative concentration of salts, due to high potential evaporation rates, but also to wet and dry deposition of marine aerosols (Adams *et al.*, 2004; Benito *et al.*, 2010). Given the geological age of Namaqualand, typically Paleo- to Neo-Proterozoic, long-term weathering of silicate dominated aquifer host rocks may also be an important contributor to groundwater salinity. However, the larger coastal zone of south-western Africa, extending into Namibia, experiences similar climatic conditions and has a comparable geological profile but groundwater salinisation is not as significant, suggesting that there are other factors at play.

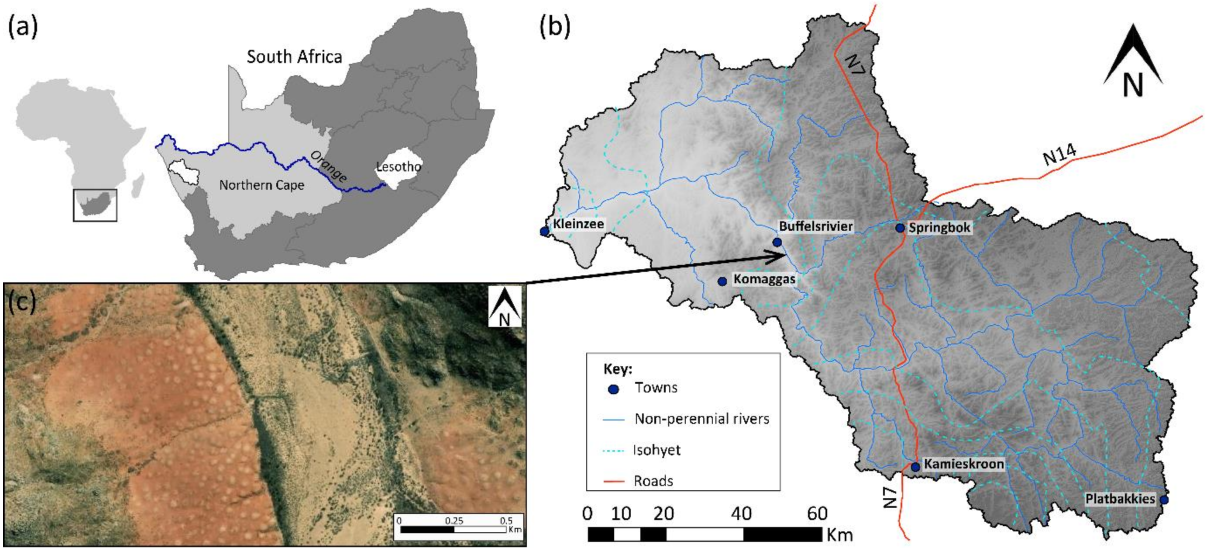

Figure 2. 1: Location of the study area. a) location of South Africa and location of the Buffels River catchment in South Africa and relative to the Orange River, (b) the Buffels River catchment showing the river tributaries and isohyets, (c) aerial image of a section of the Buffels River valley showing the distribution of heuweltjies. Heuweltjies are identified by the lighter circular patches on the surface while the interheuweltjies are the darker zones between the lighter patches.

The Namaqualand landscape is dominated by the abundance of large paleo to modern lenticular biophysical mounds locally called heuweltjies (little hills) that have been linked to paleo and modern termite activity (Cramer, von Holdt, Uys, *et al.*, 2017; Cramer, Innes & Midgley, 2012; Cramer & Midgley, 2015; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; Midgley, Harris, Hesse, *et al.*, 2002) (Figure 2. 1c). Heuweltjies occupy between 14 and 25% of the landscape (Lovegrove & Siegfried, 1986; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; Picker *et al.*, 2007) and are known to contain elevated levels of micro and macro elements, including salts, compared to the surrounding soils (Kunz *et al.*, 2012; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Midgley & Musil, 1990; Midgley *et al.*, 2012a). Although heuweltjies are specific to southern Africa, termite mounds the world over are associated with elevated micro and macro elements (López-Hernández, 2001; Seymour, Milewski, Mills, *et al.*, 2014). Elevated nutrient levels in groundwater in semi-arid regions of Australia have also been linked to the presence of termite mounds (Barnes, Jacobson & Smith, 1992; Harrington, Herczeg & Cook, 1999). Furthermore, many of these studies identified termite activity as a factor in generating increased permeability within the mound, leading to preferential flow paths faciliating in-situ draining and hence potential recharge to the groundwater system (Ackerman, Teixeira, Riha, *et al.*, 2007; Ahmed, Pradhan, Mansor, *et al.*, 2019; Bonachela, Pringle, Sheffer, *et al.*, 2014). Thus, heuweltjies and other termite mounds could play a significant role in influencing groundwater chemistry.

In this study, major cations and anions, $\delta^{18}O$, $\delta^{2}H$ values as well as $^{87}Sr/^{86}Sr$ ratios in groundwater were used to re-examine the hydrochemical character as well as distribution of saline groundwater in the Buffels River catchment, the largest catchment in Namaqualand, in the Northern Cape Province of South Africa (Figure 2. 1a, b). The objective is to better articulate the leading cause or causes of groundwater salinisation in the region and in particular the possible role of biogeochemical processes. Although this region of South Africa has in the past played host to numerous small to medium scale mining ventures, challenging economic conditions over the past decade have seen most of these ventures close down, leaving the local populations tied to a region with few economic possibilities exacerbated by the arid climate, and unpredictable quality and quantity of groundwater (Abiye & Leshomo, 2014; Hoffman, Allsopp & Rohde, 2007). As a consequence local communities tend to be poor with multiple social issues linked to the lack of employment opportunities (Pietersen, 2006). Identification of the dominant regional groundwater salinisation mechanism in the region is seen as necessary for the development of economic strategies to alleviate the current economic conditions and resultant societal problems. The holistic approach of this study, which looks at biogeochemical controls of groundwater salinity, may improve our understanding of similar groundwater systems in sub-Saharan Africa as well as other semi-arid and arid environments worldwide.

2.2 Environmental Setting

The Buffels River is the largest ephemeral river in Namaqualand with its catchment comprising an area of 9250 km^2 (Figure 2. 1 a, b). The headwaters are located in the Kamies Mountains on the Bushmanland Plateau and the river cuts down through the escarpment before emerging onto the Tertiary coastal plain and enters the Atlantic Ocean at Kleinsee (Marais et al., 2001a; Benito et al., 2010, 2011).

2.2.1 Climate and Geomorphology

Namaqualand is a semi-arid to arid region, climatically controlled by the Benguela upwelling system and mid-latitude westerlies (Weldeab, Stuut, Schneider, *et al.*, 2013). Daily temperatures in summer often exceed 35°C, while the daily maximum temperature during winter averages 17°C, reaching sub-zero at night (Davis *et al.*, 2016). The Buffels River catchment is a winter rainfall regime and mean annual precipitation (MAP) is highly variable. Inland mountainous areas in the catchment have a higher MAP than the low-lying coastal areas due to orographic effects (Benito, Thorndycraft, Rico, *et al.*, 2011; Pietersen, Titus & Cobbing, 2009; Titus, Beekman, Adams, *et al.*, 2009). The coast itself is hyper arid with a MAP of 50 mm/year while the MAP on the coastal plain towards Komaggas is higher at 110 mm/year (Figure 2. 1 b). The MAP for the Kamies Mountains, the highest elevation in the Buffels River catchment, is 400 mm/year (Benito, Thorndycraft, *et al.*, 2011; Davis *et al.*, 2016; Titus *et al.*, 2009). Heavy dewfalls occur in mid-winter while coastal fog generated by the cold Benguela current is common in summer with up to 75 fog days per year (Davis *et al.*, 2016).

Three geomorphological zones exist in Namaqualand: (1) a western coastal lowland or plain, characterised by crystalline basement rocks overlain by younger sedimentary rocks and sands; (2) an escarpment zone of exposed granitic domes, interspersed with thick layers of weathered material cut by alluvial paleochannels; and (3) the gently undulating Bushmanland Plateau consisting of erosional and aggradational phases (Adams *et al.*, 2004; Titus *et al.*, 2009). Heuweltjies, large circular mounds, generally up to 30m in diameter, but as wide as 50m, and up to 3 m high, are prominent surface features throughout the region, and have increased permeability because of biological activity of various endemic animal species (Lovegrove & Siegfried, 1989). Due to the composition of the heuweltjie soils, they are noticeably lighter in colour and are associated with distinct vegetation cover (Francis, Ellis, Lambrechts, *et al.*, 2013; Midgley *et al.*, 2002; Picker *et al.*, 2007). As a result, heuweltjies are easily discerned on satellite images due to their visual contrast with the surrounding soils. They are particularly concentrated in the lower lying valley areas throughout the Buffels River catchment.

2.2.2 Geology

The geology of the Buffels River catchment is dominated by the Bushmanland Subprovince (BSP) of the Namaqua Sector of the Namaqua-Natal Metamorphic Province (Figure 2. 2). The dominant rocks of the BSP are Mesoproterozoic granitic gneisses of the Little Namaqualand Suite (1.21 – 1.19 Ga) and the Spektakel Suite (1.09 – 1.03 Ga) (Figure 2. 2). Both suites are highly radiogenic with modern $^{87}Sr/^{86}Sr$ ratios up to 0.90000 (Clifford, Gronow, Rex, *et al.*, 1975; Yuhara, Kagami & Tsuchiya, 2001). The Little Namaqualand Suite consists of deformed ortho-gneisses including biotite-bearing granitic augen gneisses with strongly recrystalised K-feldspar. Several of the main plutons, including the Mesklip and Modderfontein Granitic Gneiss as well as the Concordia Granites occur in the study area. The Spektakel Suite does not occur in the study area. The Gladkop Suite, an older Paleoproterozoic sequence of granitic and migmatitic gneisses, occurs towards the north of the catchment. The younger

Paleoproterozoic and Mesoproterozoic supracrustal rocks of meta-sedimentary and meta-volcanic origin, the Bushmanland and Kamiesberg Groups, occurs mainly in the south of the catchment with minor outcrops towards the north (Bailie, Abrahams, Bokana, *et al.*, 2019; Macey, Bailie, Miller, *et al.*, 2018). Also within the BSP are large expanses of generic "pink gneiss" called the Lekkerdrink Gneiss for which the parental material is uncertain but is likely to be some type of quartzo-felspathic igneous protolith (Macey, Siegfried, Minnaar, *et al.*, 2011). In contrast to the escarpment and inland areas, the coastal plain along the western margin of southern Africa is dominated by more recent sedimentary deposits and has experienced multiple phases of transgression and regression followed by various periods of aeolian sediment accumulation, mostly in the last 100 Ka (Corbett, 1996; Pether et al., 2000; Roberts et al., 2006, 2014, 2009). As a result, kaolinized and deeply weathered quartzo-feldspathic, paleochannel and fluvial sediments forms part of the base of the sediment record and are overlain by Tertiary marine packages of the Buffels Marine Complex (Pether et al., 2000; Roberts et al., 2006) and younger aeolian sediments (Roberts *et al.*, 2014, 2009).

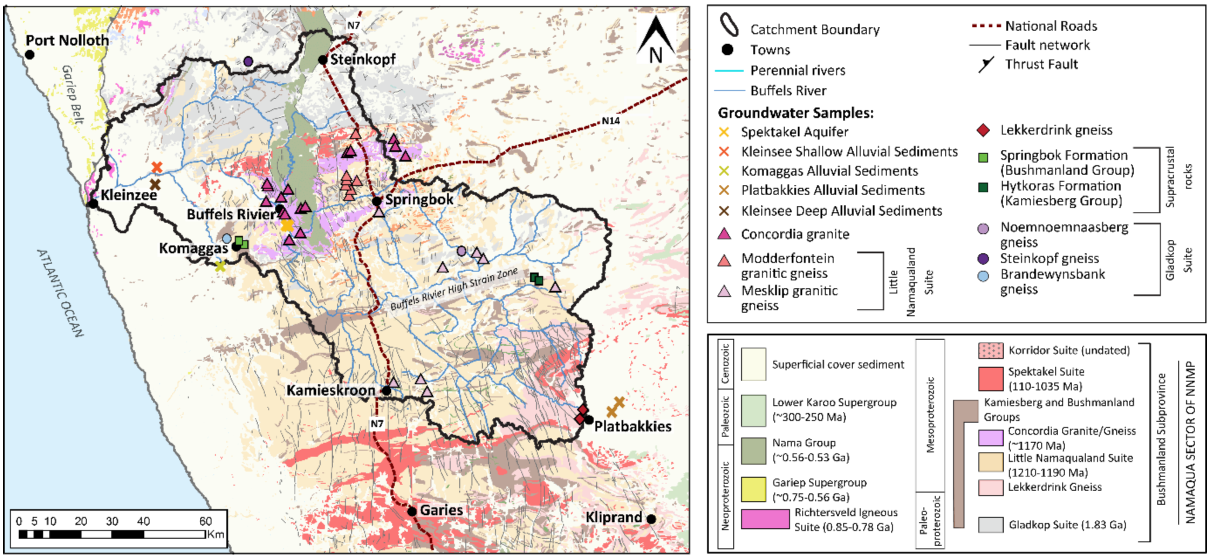

Figure 2. 2: Geological map of the study area (based on Macey et al., 2018) with the Buffels River tributaries and groundwater sample locations.

2.2.3 Hydrogeology

Groundwater in the Buffels River catchment is hosted in alluvial and fractured rock aquifer systems. The shallow alluvial aquifers result from alluvial fill discontinuities in the river valley which are further segmented into smaller aquifers by the irregular surface of the underlying basement gneisses (Benito, Thorndycraft, *et al.*, 2011). Only two of the alluvial aquifers are thought to be of any significant size and these are the Spektakel aquifer (no relation to the Spektakel Granite Suite) and the Kleinsee aquifer, both of which occur in the low-lying coastal plain. The 4-20 m deep alluvial Spektakel aquifer, which is the primary source of water to the town of Buffelsrivier, forms part of an approximately ~15 km long sand-filled basin in the Buffels River valley at the edge of the coastal plain, underlying the town of Buffelsrivier (Benito, Thorndycraft, *et al.*, 2011; Marais, Agenbacht, Prinsloo, *et al.*, 2001a,b)(Adams *et al.*, 2004; Benito, Thorndycraft, *et al.*, 2011). The Kleinsee aquifer, also a sand-filled aquifer of approximately 12 m deep, is situated at the mouth of the Buffels River. Here the aquifer feeds into the Buffels Estuary which remains relatively fresh as it is protected from the Atlantic Ocean by a sand berm which is rarely broken by the sea (Massie & Hutchings, 2018). Both of these alluvial aquifers are closely interlinked with deeper fractured bedrock aquifer systems via weathered zones that serve as pathways or conduits for subsurface intergranular flow from the shallow alluvial aquifers to the deeper granitic, gneissic and bedrock aquifers (Benito, Thorndycraft, *et al.*, 2011; Marais *et al.*, 2001a,b).

2.3 Methods and Materials

Groundwater samples were taken from existing infrastructure whilst soil samples were taken using a hand auger both on and off heuweltjies near the sites of groundwater samples. Groundwater samples were grouped based on the surface geology at the location of the borehole as defined in Figure 2. 2 and given in supplementary Table 1, although it is possible that the underlying geology at depth may vary. Specific sample locations are given in Supplementary Figure 2. 1

2.3.1 Sample Collection

A total of 48 groundwater samples were collected between March and September 2018 from boreholes, wells, and natural springs for analysis of major ion chemistry, δ^2H, $\delta^{18}O$, and $^{87}Sr/^{86}Sr$ ratios. Boreholes were existing production boreholes but the borehole infrastructure varied, and each borehole had a different pumping regime. To account for this, all boreholes were purged until EC had stabilised before sampling. EC and pH in the field were measured using Extech EC600 field probes that were calibrated on a daily basis. pH was calibrated using pH 4, pH 7 and pH 10 calibration solutions while EC was calibrated against 1413 µS/cm and 12880 µS/cm solutions. All probes were rinsed with Milli-Q water between measurements. Groundwater samples major ion chemistry, stable isotopes and Sr isotopes were filtered through 0.45 µm cellulose acetate filters into clean polypropylene (PP) conical tubes. Sample containers were filled with no headspace and kept at ~4°C with minimum light exposure until analysis.

Soil samples were collected from 14 heuweltjies and the immediate area around the heuweltjie, hereafter referred to as interheuweltjie, by means of a hand-held auger. Heuweltjies were sampled at five points, a centre point and four points at an approximately halfway point between the centre and the edge of the heuweltjie, in the north, south, east, and west directions. Interheuweltjies were also sampled in the north, east, south, and west axes of the heuweltjie. The initial intention was to collect from each sampling point on the heuweltjies, a sample from the surface, at 10-20 cm depth, at 50 cm depth, and at 100 cm depth. However, in a number of cases, a duripan layer was encountered (locally called Dorbank), which was too hard to auger through, and the samples were taken at different depths until this duripan layer was encountered (see supplementary Table 3 for depths). The hardpan layer is typically shallow in the interheuweltjie (~5 cm depth), and deeper in the heuweltjies (~ 40-50 cm depth). All samples were placed in clear plastic bags and sealed to prevent contamination.

2.3.2 Sample Preparation

Immediately upon return from the field, samples for cation and $^{87}Sr/^{86}Sr$ analysis were acidified with concentrated ultrapure HNO_3 acid (Appelo & Postma, 2005). Soil samples (heuweltjie and interheuweltjie) were dried and then lightly crushed in a mortar and pestle before being sieved through a 2 mm sediment sieve. Soils were prepared in a 1:5 soil solution ratio using MQ water and placed on a shaker for 30 minutes after which the samples were allowed to stand for 30 minutes for the soil to settle. The samples were then analysed for EC by placing a Jenway 4510 EC probe directly into the solution above the settled soil.

2.3.3 Analytical Techniques

In the laboratory, EC of both groundwater and water extracts was measured using a Jenway 4510 conductivity probe. Alkalinity and pH were measured by means of a 702 SM Titrino auto-titrator. For groundwater samples, field EC and pH results were compared to the lab results to ensure that the results were coherent. Major cations were initially analysed at the ICER laboratories in Debrecen, Hungary by means of an Agilent 8800 ICP-MS MP-AES and an Agilent 4100. Sr and a duplicate set of basic cation analyses were completed in the Central Analytical Facility (CAF) at Stellenbosch University, South Africa by means of an Agilent 7700 ICP-OES. The basic cation analyses done at the CAF laboratories were used for quality control purposes. Anion analyses were completed at the ICER facilities in Hungary by means of ion chromatography. Of the 48 samples, 36 had a charge balance of less than 10%, with the average charge balance across the dataset being -5.65. Although nitrate was analysed in these samples, the data is regarded as unreliable owing to the time between sample collection and analysis and is not included in the analysis presented here (~ 2 weeks).

Stable isotopes of oxygen and hydrogen were determined using a Los Gatos LWIA at ICER, Debrecen and reported as $\delta^{18}O$ and $\delta^{2}H$ in standard per mill (‰) notation. Internal institute water standards are calibrated to the V-SMOW, SLAP and GISP standards and reported relative to VSMOW. Analytical uncertainties of the measurements were 0.1‰ and 1.2‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively.

Strontium isotope sample preparation and analyses were performed at the University of Cape Town, South Africa. Based on Sr elemental concentration, appropriate volumes of individual groundwater samples were dried down, typically 2 – 10 ml. A few drops of concentrated HNO_3 was added to the resulting precipitate from each aliquot, followed by a second drying cycle. Finally, 1.5 ml of 2M HNO_3 was added to each Teflon vial and samples loaded onto Sr.Spec columns for standard Sr elemental separation chemistry (after Pin et al., 1994). The collected Sr fractions were dried down, re-dissolved in 0.2% HNO_3 and diluted to Sr concentrations of ±200 ppb. Samples were analysed for $^{87}Sr/^{86}Sr$ ratios using a NuPlasma HR multi-collector-ICP-MS and all data referenced to bracketing analysed of NIST SRM 987 using an $^{87}Sr/^{86}Sr$ reference value of 0.710255. The $^{87}Sr/^{86}Sr$ data are corrected for instrumental mass fractionation using the measured $^{86}Sr/^{88}Sr$ ratios, a known value for this ratio of 0.1194 and the exponential law. The isobaric interference of ^{87}Rb at 87amu is corrected using the measured signal for ^{85}Rb and the natural $^{85}Rb/^{87}Rb$ ratio.

2.3.4 Geophysics

A Geonics EM-38 MK2, a non-invasive instrument measuring surface and near surface conductivity (Bennett & George, 1995; Ding & Yu, 2014; Feikema & Baker, 2011), was used to characterise soil salinity of an area of 76.5 m x76.5 m across 3 heuweltjies in the Buffels River valley . A set of markers were placed in a grid on the surface to guide the survey. Survey lines were spaced every 5 meters to ensure full coverage. The instrument was held approximately 10 cm above the surface as the operator walked across the marked-out area. The electrical conductivity and magnetic susceptibility of the soils were measured during the survey. The sampling interval (5 seconds) of the EM 38 meant that there was a general bias being introduced in one direction (the walking direction) in contrast to the grid spacing interval (5 m). To account for directional bias in the measurements, a semi-variogram model was fitted in various directions, with 30-degree intervals, to incorporate measurement anisotropy. A wave (Hole Effect) model was the best fitted semi-variogram and accounted for the histogram developed for the sampling points. A low pass Gaussian filter was also used to reduce the bias in the sampling direction and to reduce outliers in the sampling points. Finally, the edges of the grid were trimmed, and outliers patched with data from surrounding points.

2.4 Results

2.4.1 Groundwater

2.4.1.1 Hydrochemistry

Hydrochemistry, stable isotope and Sr isotope results are given in supplementary Tables 1 and 2. Groundwater in the Buffels River catchment is variably saline with EC values ranging between 230 µS/cm and 5556 µS/cm. Groundwater hosted in the sediments around Platbakkies and Kleinsee generally had the highest EC values with sample KZ01 having the highest EC, while the sample with the lowest EC, KK01, was collected from a borehole tapping the granite basement (Mesklip Granitic Gneiss of the Little Namaqualand Suite) towards the Kamies Mountains. Of the samples collected from granitic host rocks, samples collected from the Mesklip Granitic Gneisses (n= 8) had the lowest EC overall (Figure 2. 3a), while samples from the Concordia Granites (n= 16) showed the largest variation. Two groundwater samples were classified as having come from the Lekkerdrink Gneiss but the EC of these two samples was quite different resulting in a skewed plot (Figure 2. 3a). The EC range from the Gladkop Suite groundwater (n = 3) was relatively small with EC values similar to slightly higher than the average groundwater EC of the catchment. Groundwater EC in samples from the Modderfontein Granitic Gneiss (n = 7) was more comparable with the supracrustal rocks (Kamiesberg and Bushmanland Groups) having a slightly higher overall EC.

For all groundwater samples, pH values range between 6.24 and 8.73. There was considerable variation in pH in the groundwater collected from the Concordia Granites, with pH values ranging between 6.30 and 8.73. The upper limit of the pH across the samples collected from the Lekkerdrink Gneiss, supracrustal rocks and the Gladkop Suite was comparable at ~ 7.5, while the lower pH limit of these samples was more variable. Groundwater from the Mesklip and Modderfontein Granitic Gneiss generally had lower pH values (~ 6.24 to 7.29) while the groundwater from the Concordia Granites was more variable with one outlier at a pH of 8.73 (Figure 2. 3b). The pH values from groundwater hosted by the alluvial sediments were also highly variable. Higher pH values (7.12 to 7.57) were recorded in groundwater from the Spektakel aquifer and the Platbakkies alluvial sediments with the exception of one sample from the Spektakel aquifer that had a lower pH of 6.66. Groundwater from the shallow Kleinsee sediments, deeper Kleinsee alluvial sediments and Komaggas alluvial sediments had lower pH values of between 6.78 and 6.91.

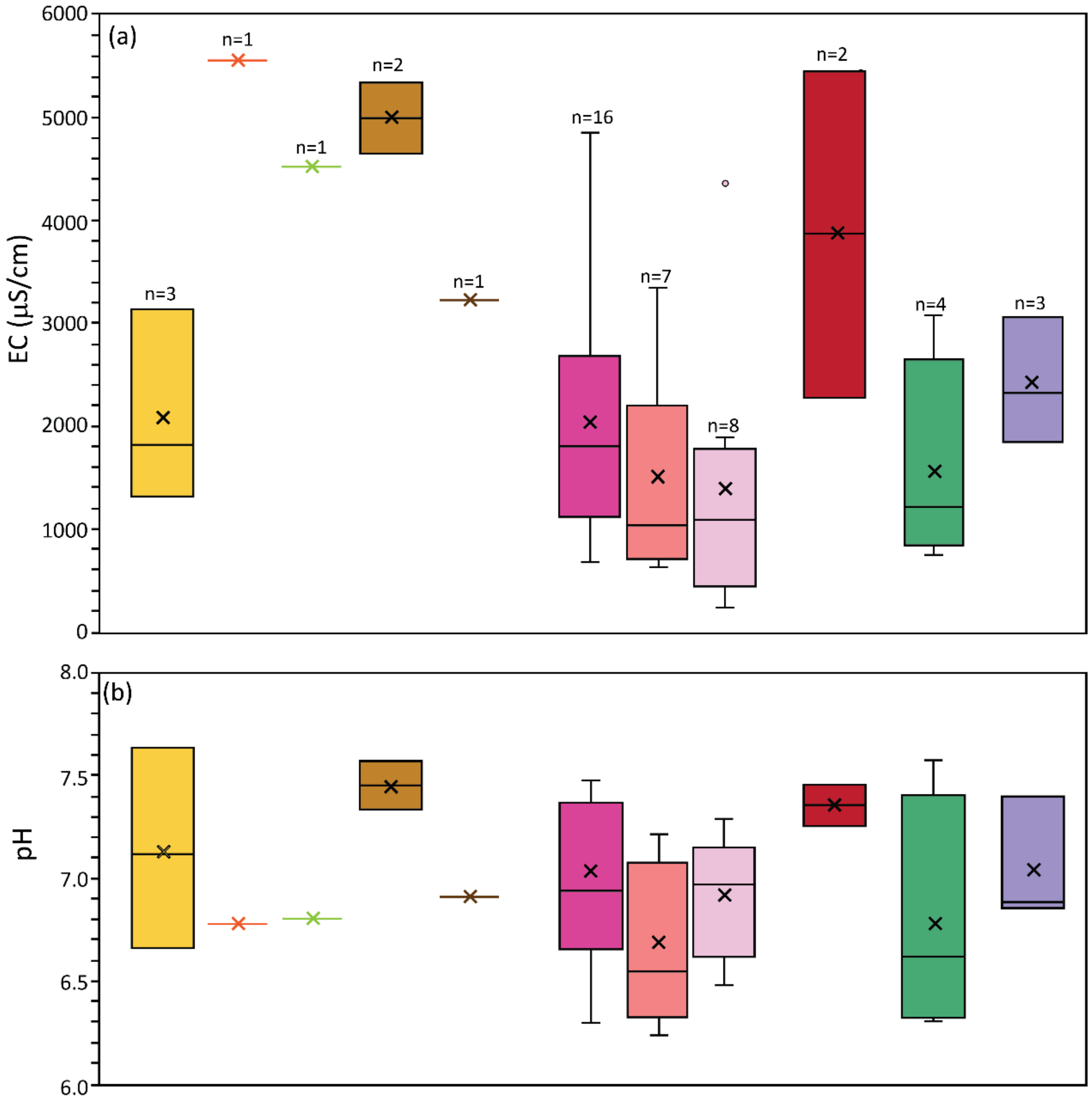

Figure 2. 3: Box and whisker plots indicating the variation in (a) EC and (b) pH in groundwater collected in from the various host rocks, an outlier sample hosted in the Concordia Granites with a pH of 8.73 was omitted from this figure due to the scaling of the diagram. Refer to Figure 2. 2 for explanation of sample colours.

Sodium and calcium were the dominant cations in groundwater in the Buffels River catchment while chloride was the dominant anion (Figure 2. 4 and Figure 2. 5). Na^+ concentrations ranged between 17.1 - 625 mg/L (mean = 200 mg/L, 1σ = 158 mg/L), while Ca^{2+} ranged between 6.16 - 340 mg/L (mean= 89.5 mg/L, 1σ = 66.3 mg/L). The concentration of Mg^{2+} and K^+ in the groundwater was lower ranging between 2.20 - 168 mg/L and 0.74 - 30.7 mg/L respectively. The major anions controlling the hydrochemistry of the groundwater were, in order of decreasing concentration, Cl^-, SO_4^{2-} and HCO_3^-, but the concentration of each anion was quite variable. The Cl^- concentrations in groundwater ranged between 10.8 - 2034 mg/L (mean = 524 mg/L, 1σ = 456 mg/L), while SO_4^{2-} concentrations ranged between 2.31 - 453 mg/L (mean = 151 mg/L, 1σ = 110 mg/L), and HCO_3^- concentrations ranged between 19.1 - 380 mg/L (mean = 119 mg/L, 1σ = 73.7 mg/L). Based on the above concentrations, groundwater in this area is dominantly a Na-Cl type, with some mixed type waters (Figure 2. 5).

Groundwater hosted in the alluvial sediments had the highest concentration of dissolved ions (Supplementary Table 2. 1). Groundwater from Platbakkies alluvial sediments in the east of the catchment contained higher dissolved ion concentrations than groundwater collected from alluvial sediments closer to the coast. Groundwater collected from the Modderfontein Granitic Gneiss, Concordia Granites and Mesklip Granitic Gneiss plot in the mixed and Na-Cl zones (Figure 2. 5). Of the samples collected from the supracrustal rocks, groundwater from the Kamiesberg Group contains higher concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- than the groundwater hosted by the Bushmanland Group, which is dominated by Na^+ and Cl^- (Figure 2. 4). The groundwater chemistry of the samples collected from the Gladkop Suite is comparable to that of the granitic gneisses. Only two samples were collected from the Lekkerdrink Gneiss, but there are significant differences in the groundwater chemistry, specifically in the Mg^{2+}, Ca^{2+} and Cl^- concentrations.

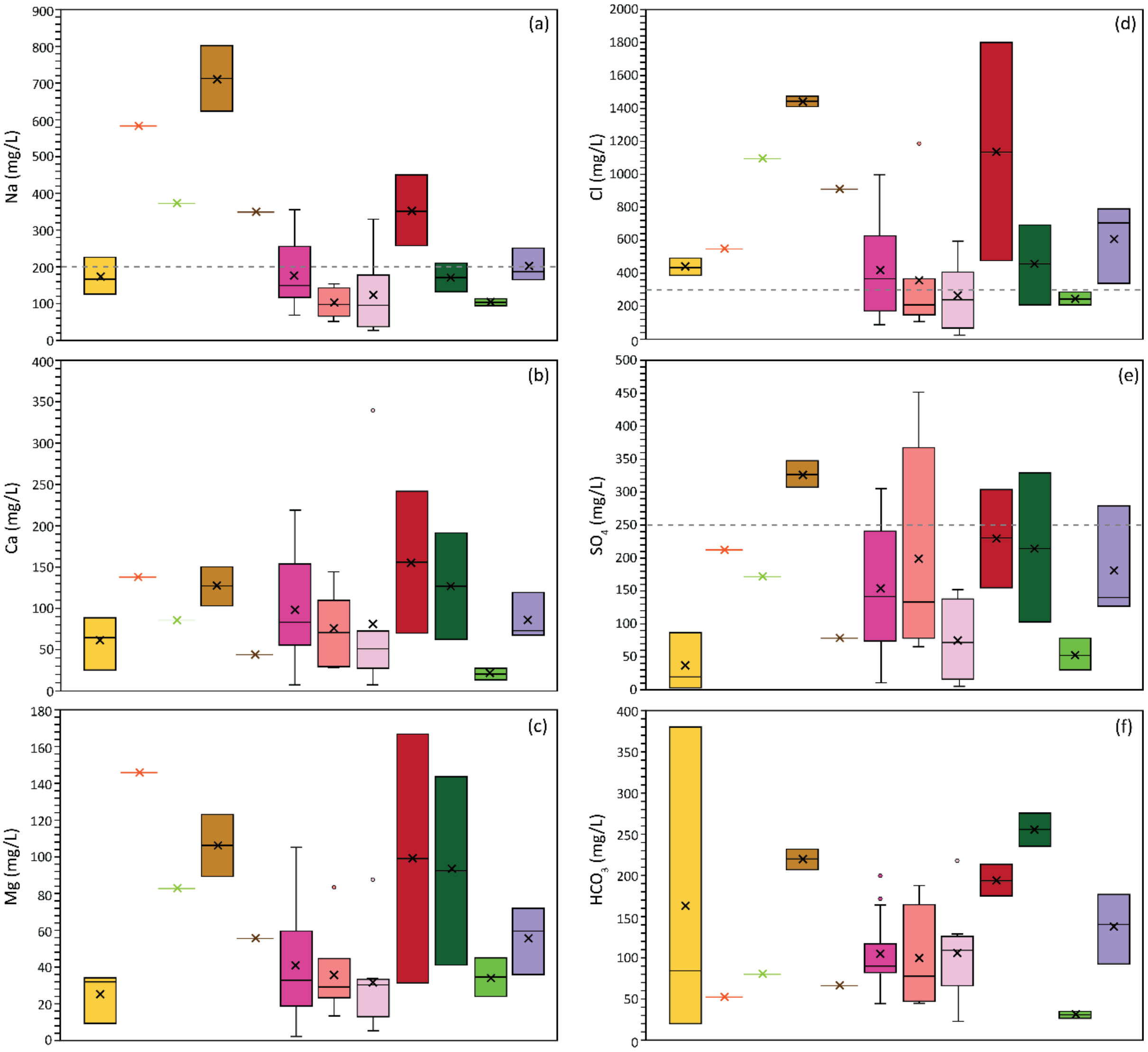

Figure 2. 4: Box and whisker diagrams of major cations and anions present in the groundwater hosted within the different rock types. The limits of the World Health Organisation standards for drinking water are shown in a grey dashed line (World Health Organisation, 2017). Refer to Figure 2. 2 for explanation of sample colours.

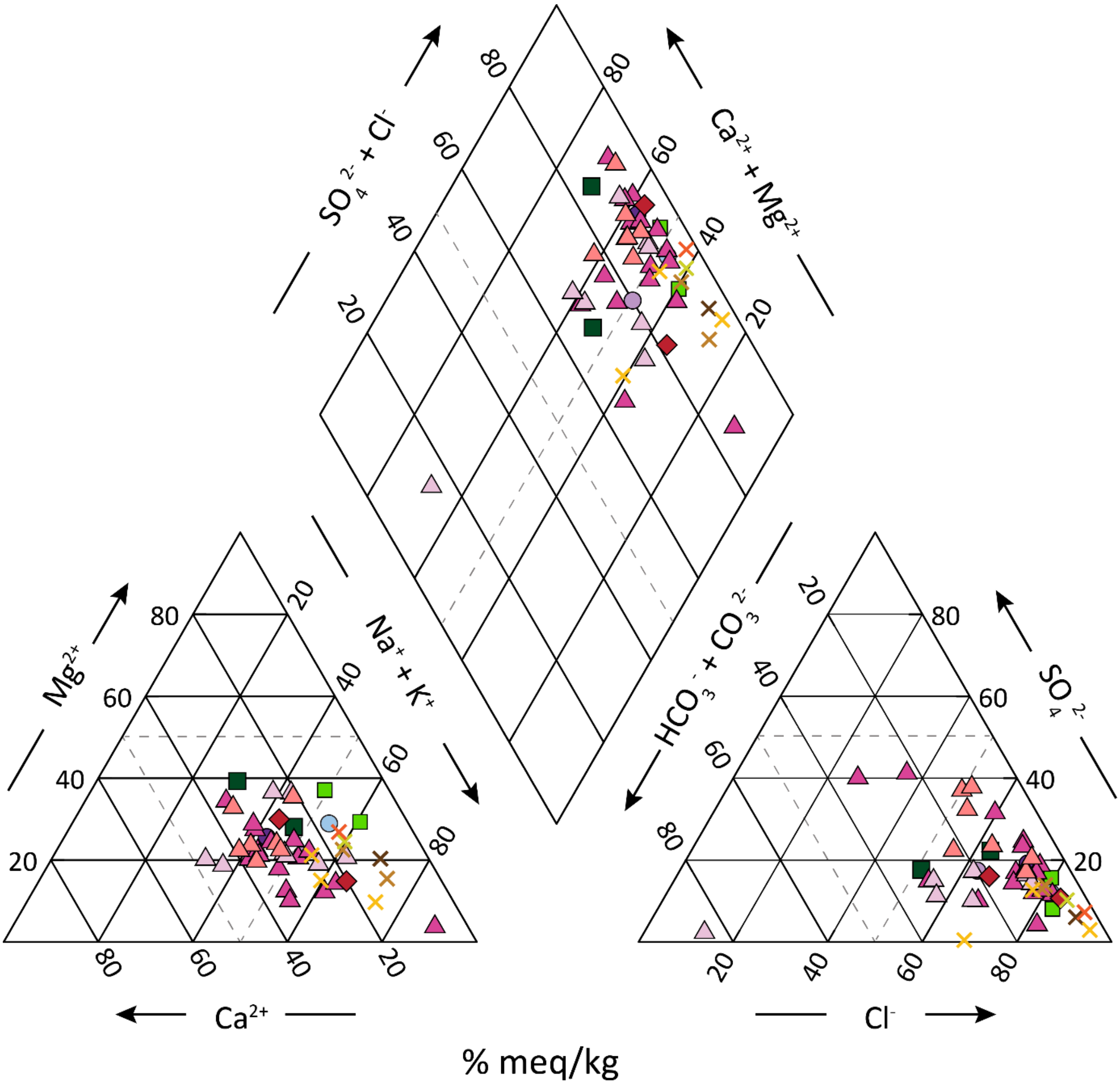

Figure 2. 5: Piper diagram indicating groundwater types. Refer to Figure 2. 2 for sample legend.

2.4.1.2 O and H Stable Isotopes

The total range in groundwater δ^{18}O and δ^{2}H values was between -5.25 ‰ and -0.53 ‰ and between –33.90 ‰ and –2.48 ‰ respectively (Supplementary Table 2. 2). These values did not appear to show a distinct evaporation trend and all the samples were close to the GMWL and did not appear to follow the LMWL (Figure 2. 6) defined by van Gend (2018). Groundwater samples collected from the Concordia Granites had less negative δ^{18}O and δ^{2}H values than those collected from the Little Namaqualand Suite including both the Modderfontein and Mesklip Granitic Gneiss. Groundwater samples hosted by the Kamiesberg and Bushmanland Group rocks varied in that samples collected from the Hytkoras Formation (Kamiesberg Group) had more negative values than those collected from the Springbok Formation (Bushmanland Group). Similarly, two groundwater samples collected from the Platbakkies alluvial sediments in the east of the catchment had more negative δ^{18}O and δ^{2}H values, while groundwater collected from other alluvial sediments had less negative δ^{18}O and δ^{2}H values. There is a general trend among all the samples, irrespective of the host rocks, where groundwater with more negative δ^{18}O and δ^{2}H values were collected furthest inland while the less negative samples were collected near the coast (Figure 2. 7).

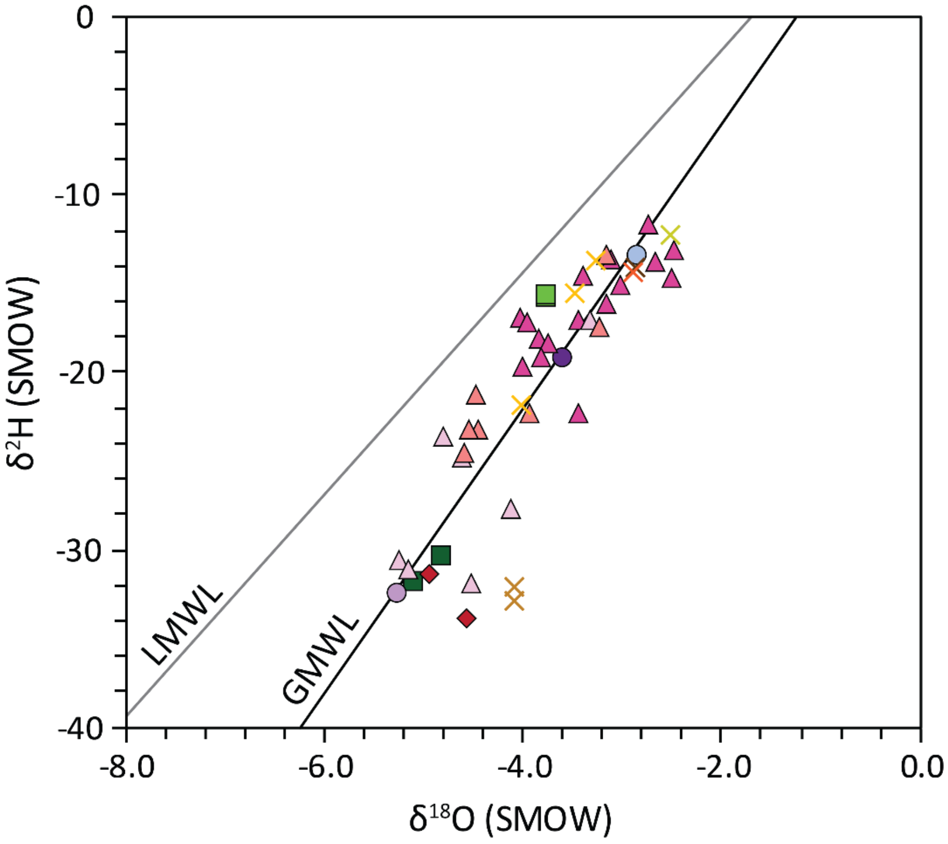

Figure 2. 6: Standard δ^{2}H vs δ^{18}O meteoric water diagram showing groundwater samples relative to the local meteoric water line (LMWL) as determined by van Gend (2017). Refer to Figure 2. 2 for sample legend.

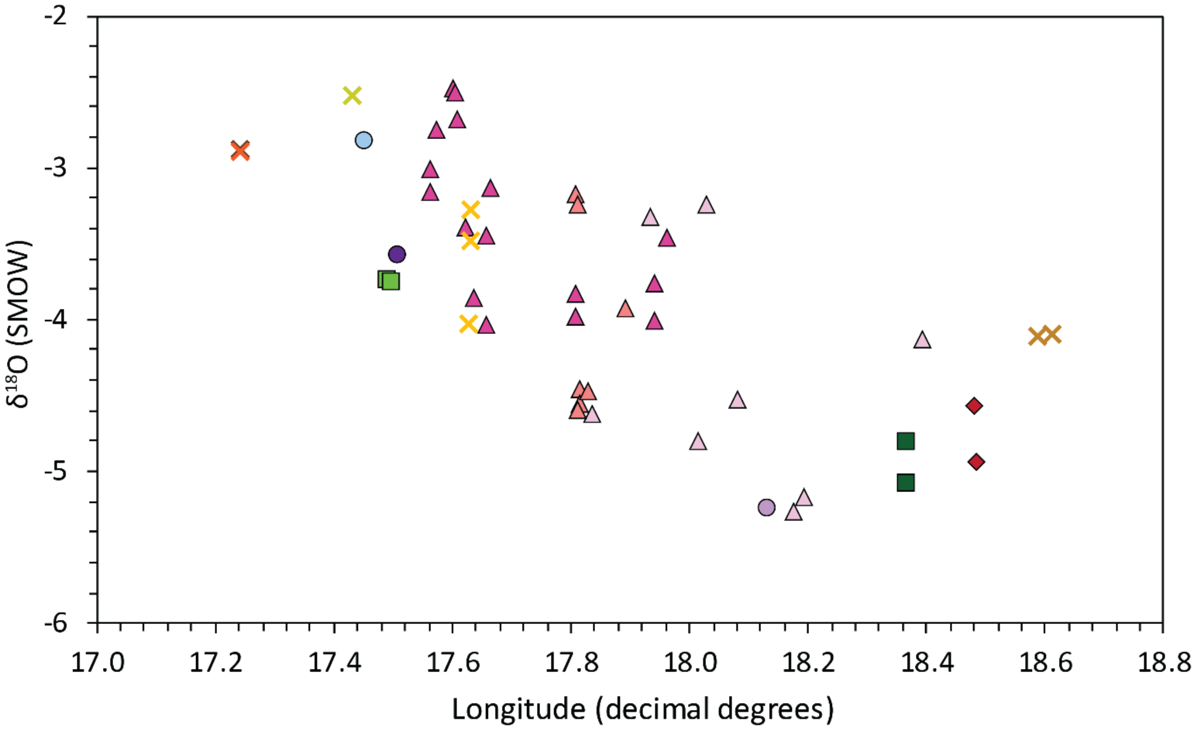

Figure 2. 7: δ^{18}O vs longitude and therefore the change in δ^{18}O relative to the coast at a longitude of between 17.0 and 17.2 decimal degrees. Refer to Figure 2. 2 for sample legend.

2.4.1.3 Sr Isotopes

^{87}Sr/^{86}Sr ratios in this area are highly radiogenic ranging between 0.71355 and 0.76934 with an average of 0.73872. Groundwater samples collected from the alluvial sediments and the Lekkerdrink Gneiss had the lowest ^{87}Sr/^{86}Sr ratios, while four of the eight samples with ^{87}Sr/^{86}Sr ratios greater than 0.75000 were collected from the Mesklip Granitic Gneiss (supplementary Table 2). Other samples with ^{87}Sr/^{86}Sr ratios above 0.75000 were collected from the Concordia Granites and the Gladkop Suite. ^{87}Sr/^{86}Sr ratios from samples collected from the Mesklip Granitic Gneiss were also the most variable as four samples had ^{87}Sr/^{86}Sr ratios above 0.7500 and four samples had ^{87}Sr/^{86}Sr ratios below 0.74000, with one as low as 0.71749. Groundwater from the Modderfontein Granitic Gneiss generally had ^{87}Sr/^{86}Sr ratios similar or slightly higher than the average ^{87}Sr/^{86}Sr ratio, while the ^{87}Sr/^{86}Sr ratios in groundwater from the Concordia Granites were above the regional ^{87}Sr/^{86}Sr average. Samples from the Bushmanland and Kamiesberg Groups had a slightly wider range of ^{87}Sr/^{86}Sr ratios (0.72915 – 0.74814) than the Modderfontein Granitic Gneiss (0.73117 – 0.74670) but the groundwater ^{87}Sr/^{86}Sr ratios were still comparable to that of the Modderfontein Granitic Gneiss (Figure 2. 8).

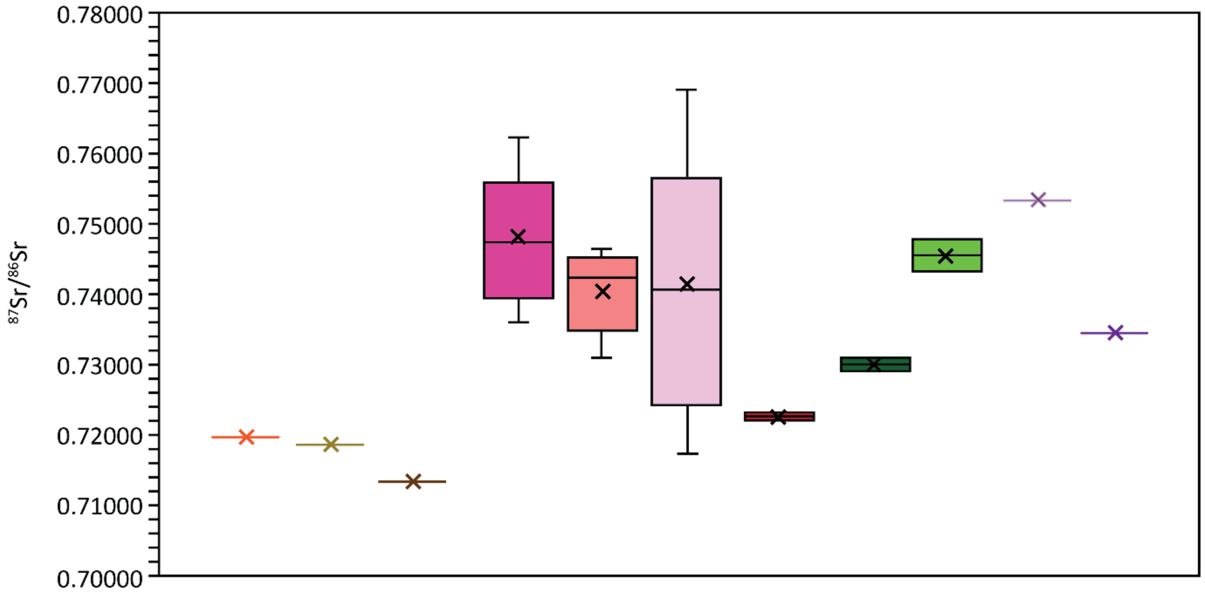

Figure 2. 8: ^{87}Sr/^{86}Sr isotope ratios for groundwater collected in the Buffels River catchment grouped according to the host rocks from which the samples were collected. Refer to Figure 2. 2 for explanation of sample colours.

2.4.2 Heuweltjies

2.4.2.1 Water soluble soil EC

Analysis of EC generated from water soluble salts from the heuweltjie soil samples indicated that EC values for heuweltjie and interheuweltjie soil were highly variable but generally the EC of heuweltjies soils was higher than interheuweltjie soils (Figure 2. 9). Furthermore, EC values of samples taken from the centre of the heuweltjies were generally higher compared to the samples taken at the mid points of the heuweltjies (supplementary Table 3). The average EC for samples collected on the heuweltjies was 3097 µS/cm, whilst for interheuweltjie samples the average EC was 283 µS/cm. The EC of samples collected from deeper in the heuweltjies was generally much higher than shallower samples. The average EC of samples collected at 75 cm or deeper was 5120 µS/cm, while the average EC of samples collected between the surface and 75 cm was 2717 µS/cm. The EC of the interheuweltjie samples followed a similar trend of increasing EC with depth, but the overall EC of the interheuweltjies was approximately 10 times less than that of the heuweltjies.

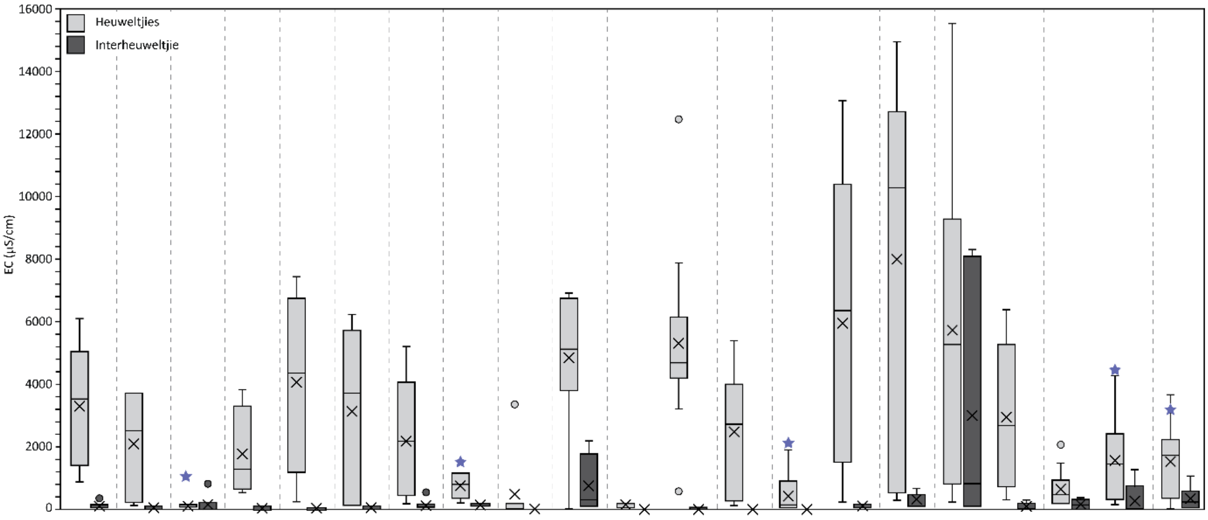

Figure 2. 9: Box and whisker plot showing the sediment EC values from samples collected from heuweltjies and interheuweltjies.

2.4.2.2 *EM Scanning*

The EM-38 scan not only shows variation in soil apparent conductivity (ECa) across the scanned area but is also provides an indication of the spatial distribution of salt concentration. ECa values range between 59.4 µS/cm and 1102 µS/cm with the highest EC values clustering together and the EC decreasing gradually from the clusters of high EC values (Figure 2. 10). When compared to aerial imagery, the zones of high ECa values are spatially related to the heuweltjies while the low ECa values fall on interheuweltjie areas. Moreover, larger areas with higher ECa values are seen at depths of 1 m compared to that of 0.5 m, suggesting an increase in ECa values with depth (Figure 2. 10a and b). The overall ECa values generated by the scans showed similar trends to what was seen in the water-soluble EC values with high EC values with the highest EC values closer to the centre of the heuweltjies, decreasing towards the interheuweltjie area. The increase in EC with depth is also consistent with the results of the water-soluble EC values.

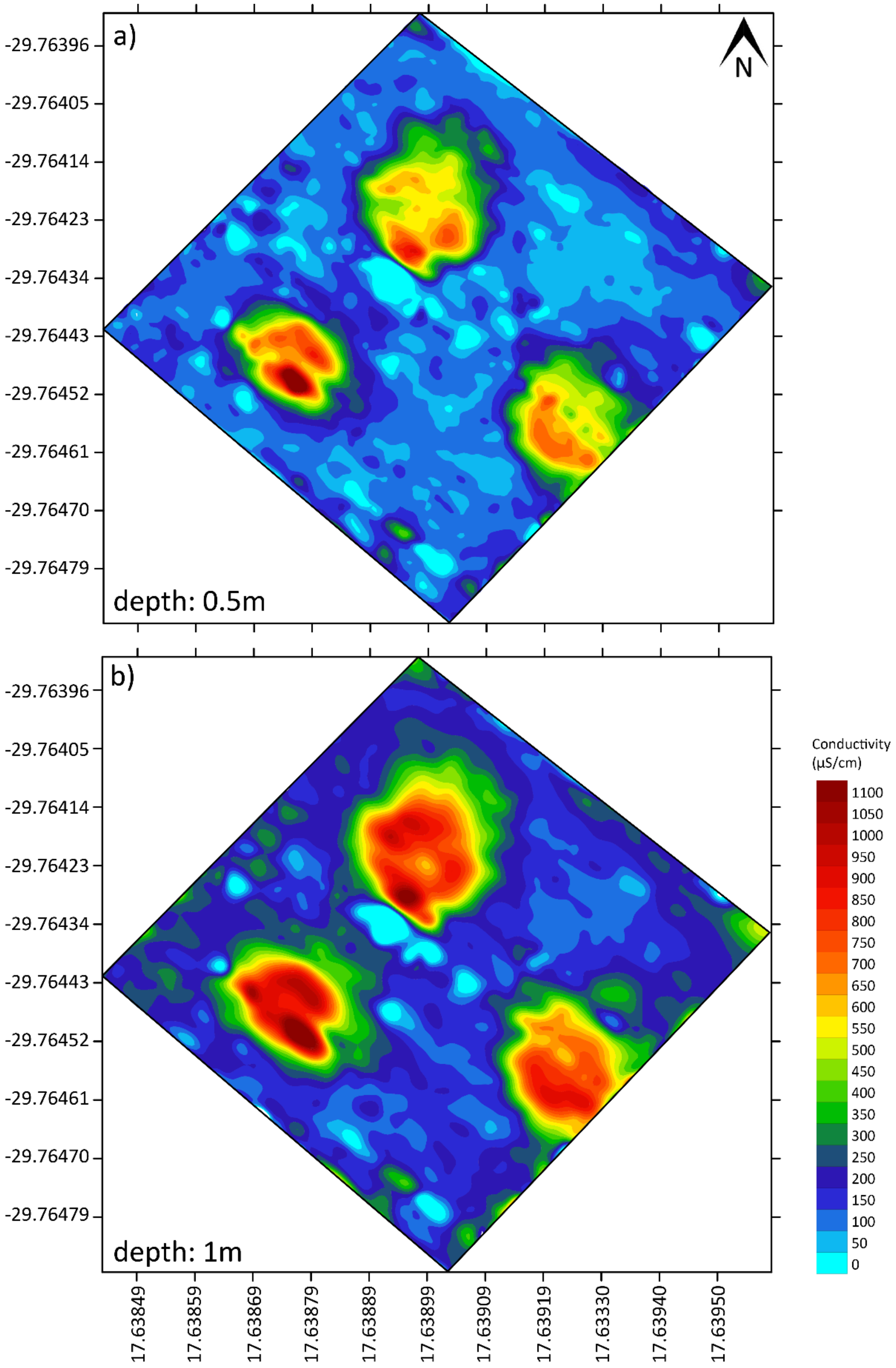

Figure 2. 10: Distribution of apparent EC (ECa) across three heuweltjies and the interheuweltjie zones in the Buffels River valley, derived by electromagnetic induction scanning measured at a) 0.5 m and b) 1.0 m below the surface. High EC values are represented in red and coincide with the heuweltjies whereas the low EC values are represented in blue coinciding with the interheuweltjie zones. Image produced by reprocessing of data originally reported by van Gend (2018).

2.5 Discussion

In the literature, groundwater in the Buffels River catchment is described as belonging to either the shallow Spektakel or Kleinsee alluvial aquifers or hosted in the basement gneisses (Adams *et al.*, 2004; Titus *et al.*, 2009). Based on the data presented above, the groundwater is far more variable in hydrochemistry than just a three-type categorisation. Moreover, even for groundwater samples that have been collected from similar host rocks, there are still substantial variations that might reflect variations in recharge pathways and flow path lengths. Nevertheless, there are commonalities in the composition of some of the groundwaters, particularly in terms of trends and patterns, rather than absolute concentrations that suggest that common processes are responsible for the elevated salt concentrations. Here we discuss the different types of groundwaters present and where salts are derived from, as well as what this might mean for the development of groundwater salinisation in the region. We suggest ways that salts may be transferred to the groundwater system and what this means for both economic development in the region as well as groundwater resilience in the face of ongoing climate change.

2.5.1 Groundwater Types and Degree of Salinity

The Kleinsee and Spektakel aquifers are the two known alluvial aquifers in the Buffels River catchment. However, Benito et al., (2010), mentioned that smaller, isolated and less significant alluvial aquifers also exist. The data in this study confirm that these smaller local alluvial groundwater systems exists. Six different alluvial systems are defined in terms of hydrochemistry and location. These include the previously documented Kleinsee aquifer system (Benito *et al.*, 2010; Massie & Hutchings, 2018) that was not sampled in the present study. The five documented in this study include: (1) deep and (2) shallow alluvial sediments approximately 20 km inland from Kleinsee; (3) Komaggas alluvial sediment; (4) the Spektakel aquifer; and (5) Platbakkies alluvial sediment. The samples collected from the shallow as well as deep sediments 20 km inland of Kleinsee are outside the range of the Kleinsee aquifer and are thus classified as a different system. The differences in hydrochemistry together with the geographical location provides evidence that the groundwater hosted in these alluvial systems are not related but rather smaller isolated systems (Figure 2. 2)

In contrast to the alluvial aquifer systems, which are isolated systems, groundwater hosted in the fractured rock aquifer systems may be connected by fractures and faults leading to interaction with different granitic or gneissic units along extended flow paths. The Kamies Mountains, the area with the highest precipitation, and thus proposed as the main recharge zone (Benito *et al.*, 2010), are dominated by the Mesklip Granitic Gneiss of the Little Namaqualand Suite. The groundwater hosted in the Mesklip Granitic Gneiss generally have the lowest concentrations of dissolved ions and the largest range (lowest to highest) of $^{87}Sr/^{86}Sr$ ratios (Figure 2. 8). In contrast to this, groundwater hosted in the Concordia Granites have a narrower range of $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ and $\delta^{2}H$ values are more positive with a shallower trend indicative of evaporation (Figure 2. 6).

The Modderfontein Granitic Gneiss is surrounded by the Concordia Granites and it was thought that the groundwater characteristics of these two groups would be similar. Whilst this is the case for the hydrochemistry in terms of cations and anions, the O, H and Sr isotopes of the two groups are dissimilar. Groundwater hosted by the Modderfontein Granitic Gneiss display a narrow range of $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$ and $\delta^{2}H$ values that generally plot as a group with more negative values than the groundwater hosted by the Concordia Granites. This suggests that the groundwater from the Modderfontein Granitic Gneiss aquifer system has a distinct flow path and/or likely different recharge zone to that of groundwater in the Concordia Granites. However, given the close geographic association of these two rock units, for the recharge zones to differ suggests that groundwater conduits within the two rock types are isolated from one another. It is more difficult to characterise groundwater hosted the Lekkerdrink Gneiss, Gladkop Suite and the supracrustal rocks because the geological units are smaller, more isolated and a limited number of samples were collected from these host rocks. Where more than one sample was collected from a specific host rock, the hydrochemistry of these samples was generally similar in character and hydrochemistry, specifically $^{87}Sr/^{86}Sr$ ratios.

Given the variability in groundwater chemistry in the Buffels River catchment, together with the complexities of the geology, it is difficult to define specific groundwater types that might reflect different aquifer systems or flow paths through the catchment. The composition of groundwater hosted in the fractured rock basement gneisses seems to be largely dependent on the specific rock type from which it is derived. Thus, for example, the composition of groundwater hosted by the Modderfontein Granitic Gneiss has a slightly different composition to groundwater hosted by the Mesklip Granitic Gneiss. Although there are variations in groundwater composition, there are general trends and patterns seen in groundwater hosted in different rocks, suggesting that the groundwater across the catchment may be affected by similar processes contributing to the salt content.

2.5.2 Where do the salts come from?

The origin of salts in natural salinisation processes is generally linked to dry deposition of marine aerosols and mineral weathering processes (Jørgensen & Banoeng-Yakubo, 2001; Karroum *et al.*, 2017; Tostevin, Turchyn, Farquhar, *et al.*, 2014; Zhang, Frape, Love, *et al.*, 2007). However, regions affected by semi-arid to arid climatic conditions, low precipitation rates and high evaporation rates leading to evaporative concentration of salts often exacerbates the salinisation process. This was previously thought to be the case in the Buffels River catchment (Adams *et al.*, 2004). In this section we discuss the role of evaporative concentration and the origin of salts, as opposed to the salinisation process, present in groundwater in the Buffels River catchment.

2.5.2.1 The Role of Evaporative Concentration

Saline groundwater in the Buffels River catchment has previously been ascribed to evaporative concentration. However, evaporation affects not just salt concentrations but other tracers of the evaporative process as well such as the stable isotopes of O and H. During evaporation, the heavier isotopes of O and H are preferentially retained in the water phase, leading to characteristic evaporative trends away from the GMWL (Figure 2. 11). These trends have been successfully modelled using the well-established Craig-Gordon model of evaporation (Craig & Gordon, 1965), and the slope of the evaporation line and the distance samples plot along this evaporation trend can be used to identify the environmental conditions under which evaporation is occurring (e.g. Gonfiantini et al., 2018). Given the very significant concentration of salts over and above the concentration in normal precipitation, one would expect there to be a distinct evaporation trend present in the O and H stable isotope data from Buffels River catchment, but this is not the case (Figure 2. 11). Taken as a whole, the samples from the Buffels River catchment are consistent with the GMWL. However, breaking the data into groups shows some possible deviation from this. In particular, taking the groundwater samples hosted by the Concordia Granites, may indicate an evaporative trend that tracks back to a starting point on the LMWL of $\delta^{18}O$ = -5.8 ‰ and $\delta^{2}H$ = -25.5 ‰. However, if this were assumed (in a simple evaporative model) to be the starting point for evaporation of precipitation in the region, the groundwater samples obtained from the Kamiesberg Group, the Lekkerdrink Gneiss, several of the Mesklip Granitic Gneiss and groundwater from the Platbakkies alluvial sediment, clearly cannot be derived from the same starting point as they are significantly lower on the GMWL. These compositions likely imply groundwater sourced from a wetter or colder climate and may rather represent groundwaters that were recharged further back in the past. This trend of more negative $\delta^{18}O$ and $\delta^{2}H$ values from prior to 6000 years ago has previously been documented across Southern Africa (Heaton, Talma & Vogel, 1986; Kulongoski, Hilton & Selaolo, 2004).

In addition to the above, examination of the $\delta^{18}O$ and $\delta^{2}H$ values from the alluvial aquifer systems in the Buffels River valley, the Spektakel and shallow Kleinsee as well as Komaggas alluvial aquifers, systems that are demonstrably shallow and likely to be affected by evaporation, do not define an evaporation trend, plotting instead along a trend more consistent with the GMWL. Based on the above, it seems unlikely that evaporation, either directly from precipitation or from pore water stored after precipitation, is a big contributor to the presence of salt in the Buffels River groundwater. This is similar to patterns documented by Abiye and Leshomo (2013) who also found no distinct evaporative signal in groundwater from the eastern part of the Buffels River catchment, but a distinct evaporative signal in groundwater from the next catchment towards the east. Based on this analysis, it would appear that other sources of salt must be considered.

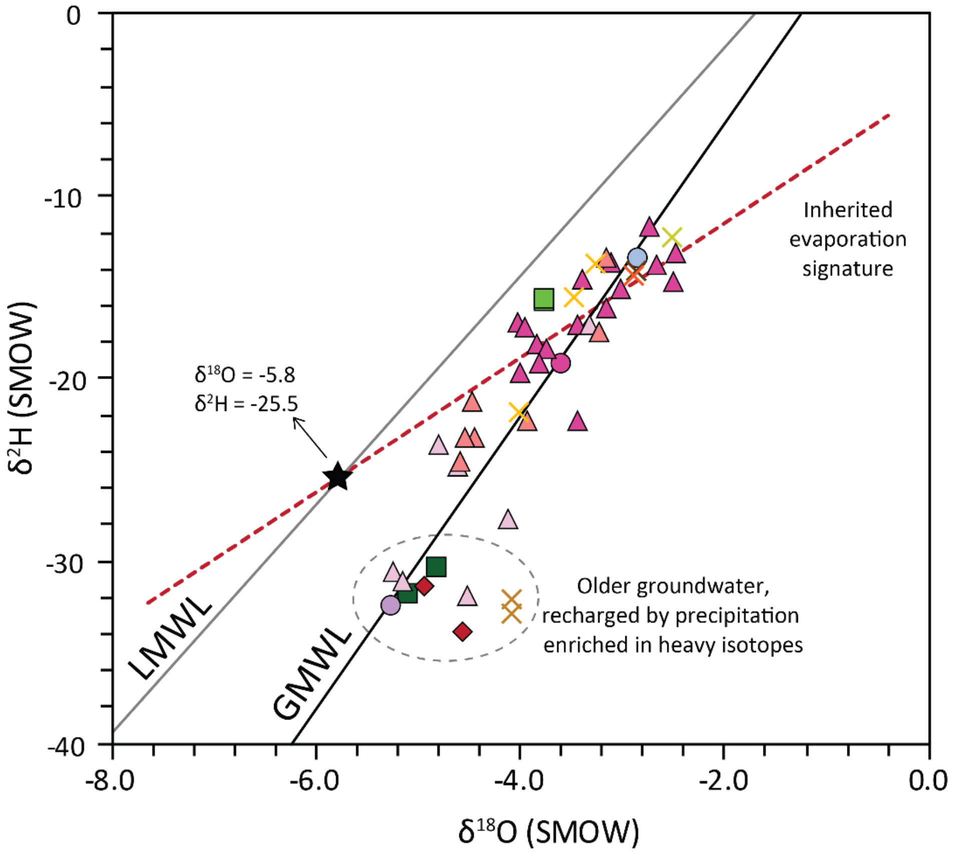

Figure 2. 11: δ^2H vs δ^{18}O showing the more negative group of samples, which may be older, and the inherited evaporation line of groundwater hosted in the Concordia granites. Refer to Figure 2. 2 for sample legend.

2.5.2.2 *Sea spray and marine aerosols*

Marine aerosols are transported inland from the coastal zones through atmospheric currents and are incorporated into the groundwater system in two ways; 1) aerosols are washed from the atmosphere during a rain event and transported into the aquifer system via recharge and 2) deposited on land surfaces and vegetation as a result of evaporation. Precipitation events will cause dissolution and percolation of salts into the groundwater system (Gamboa *et al.*, 2019). Na and Cl are the most abundant ions in seawater with a molar ratio of Na^+/Cl^- of 0.86. However, during evaporation of the liquid phase of the aerosols deposited on the soil/vegetation surface, Na and Cl ions accumulate in the form of halite (NaCl) with a Na^+/Cl^- molar ratio of 1 (Magesh, Botsa, Dessai, *et al.*, 2020). Aquifer systems affected by only halite dissolution will have Na^+/Cl^- molar ratios of 1 while those affected by direct input of only marine aerosols will reflect lower Na^+/Cl molar ratio of 0.86 (Möller, 1990). In coastal regions, with semi-arid to arid climates, it is likely that potential recharge is affected by both of these processes before it infiltrates the soils. These signals are often disguised as both the atmospheric and dissolved ions pass through the soil during which ion exchange reactions, adsorption of Na to clay surfaces, will affect the composition of the recharge water by reducing the Na/Cl ratio in both cases. Cation exchange reactions are particularly prominent in clay forming rock types (granites for example) where in conditions of increased ionic strength, monovalent cations such as Na are preferentially adsorbed, therefore, decreasing the concentration of dissolved Na (Jalali, 2007). Given that there is not a strong evaporation signature in the stable isotope data of the groundwater in the Buffels River catchment and that the Na/Cl ratios of the groundwater are generally not equal to 1 (Figure 2. 12), it is likely that salts originated as a result of dry deposition of marine aerosols that accumulated on the land surface. Over time these salts were transported into the vadose zone where the groundwater composition was affected by cation exchange reactions and from there could have migrated to the deeper groundwater system (Figure 2. 12).

Reference data from two smaller quaternary catchments, F30A in the Buffels River catchment and D82B, adjacent but to the east of the Buffels River catchment from Abiye and Leshomo (2013), are displayed as open circles on Figure 2. 12. Data from catchment F30A (quaternary catchment in the larger Buffels River catchment) follows a similar trend to the groundwater collected in this study and was found to be a result of dry deposition of marine aerosols and mineral weathering, while the groundwater in catchment D82B (outside of the Buffels River catchment) shows a more lateral trend, interpreted as an effect of evaporation.

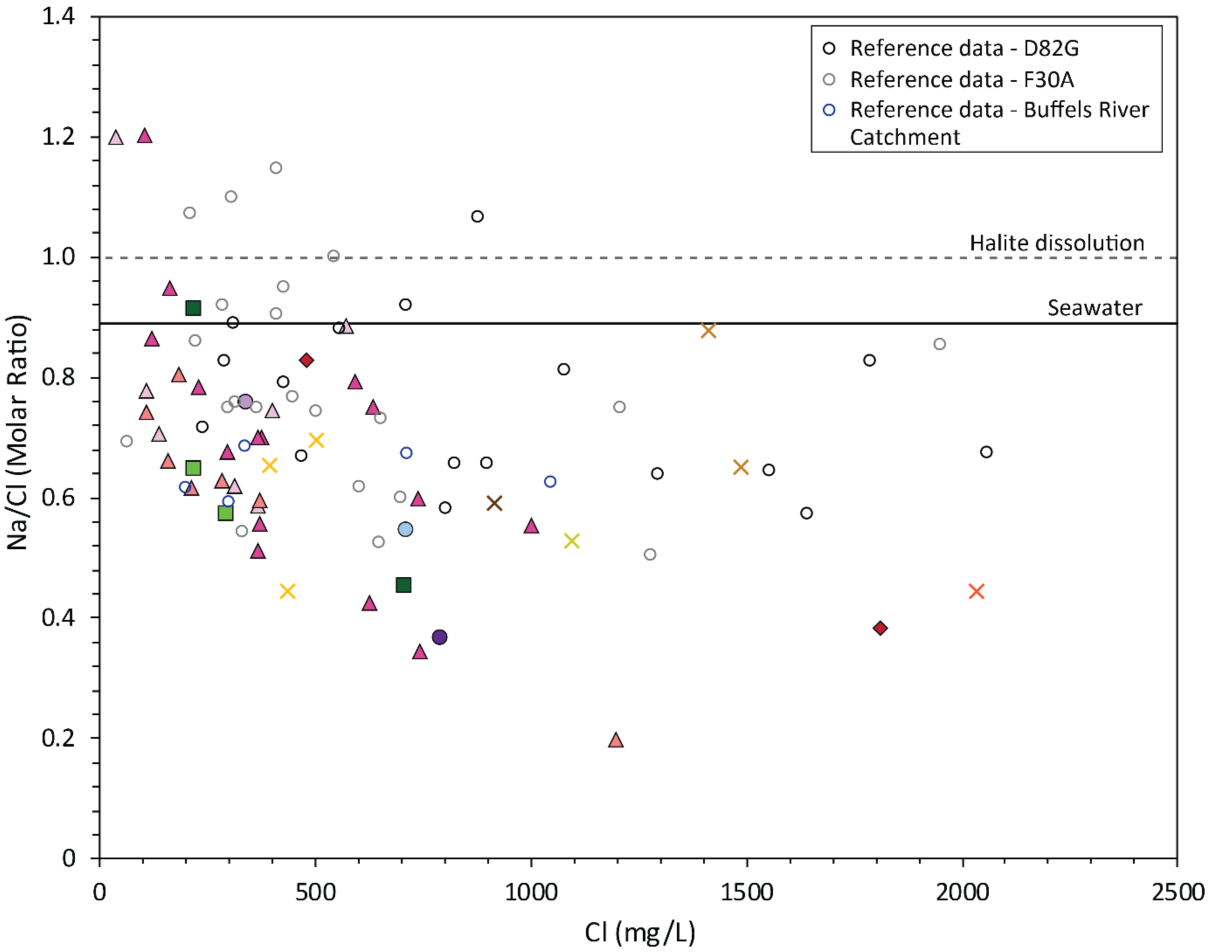

Figure 2. 12: Na/Cl ratio vs Cl concentration of groundwater sampled in the Buffels River catchment. Reference data represented as open circles taken from Abiye and Leshomo (2013) and Petronio (2017). Refer to Figure 2. 2 for sample legend.

2.5.2.3 *Water-rock interaction and mineral weathering*

Water-rock interaction and weathering of silicate rocks can play a significant role in controlling the water chemistry of the groundwater. Elevated Na, K and Ca together with elevated $^{87}Sr/^{86}Sr$ ratios in groundwater are linked to dissolution of feldspar minerals which are common in granitic environments (Santoni *et al.*, 2016). Groundwater $^{87}Sr/^{86}Sr$ ratios in the Buffels River catchment are directly related to the aquifer host rock, with both the alluvial and fractured aquifer systems indicating specific $^{87}Sr/^{86}Sr$ ratios. Furthermore, there are distinct differences in groundwater chemistry between the groundwater hosted within different supracrustal, granitic or gneissic fractured aquifer systems. Groundwater with elevated $^{87}Sr/^{86}Sr$ ratios are typically hosted by the Concordia Granites and Little Namaqualand Suite gneisses, which are known to be highly radiogenic rocks.

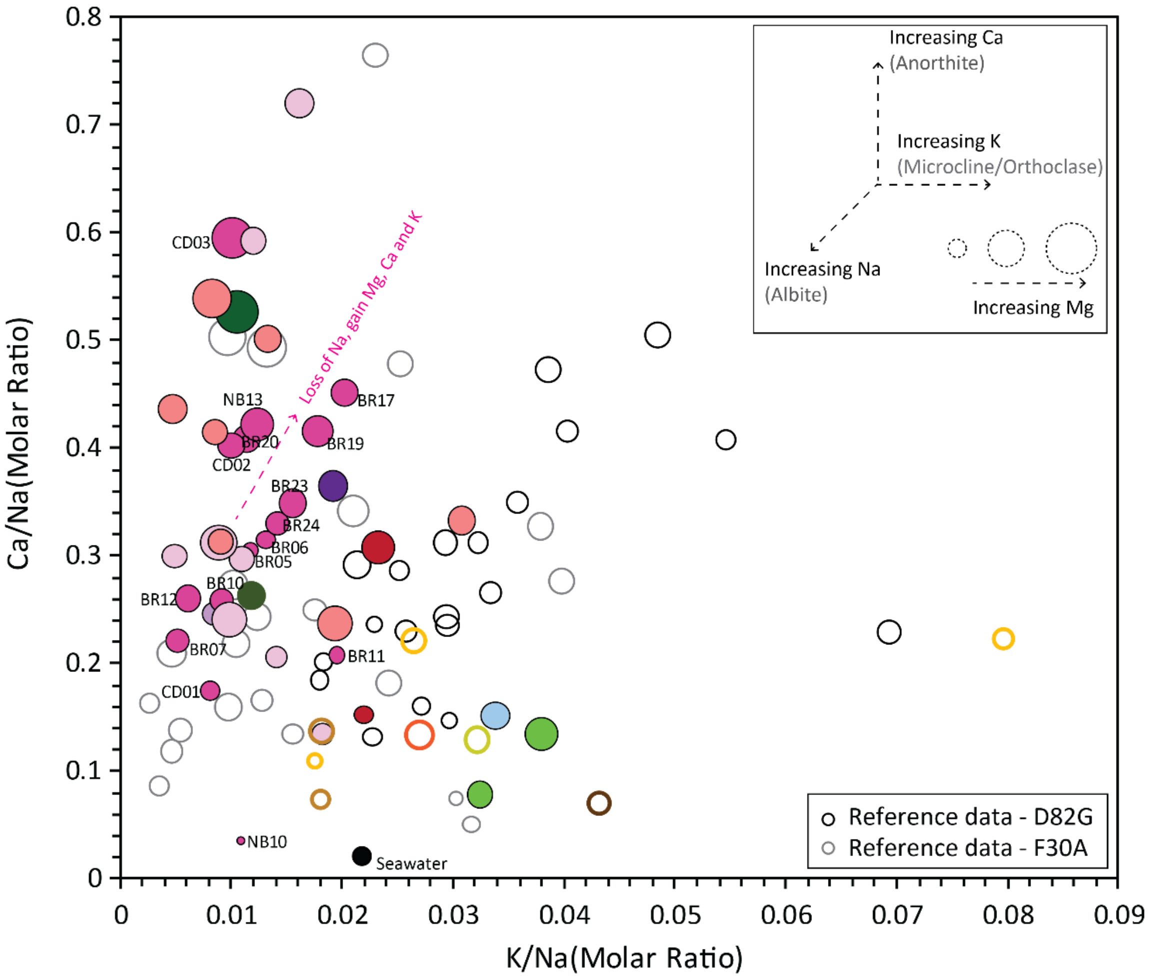

Figure 2. 13: Plot of Ca/Na ratio vs K/Na ratio with the symbol size proportional to the Mg/Na ratio. Mg/Na ratios range between 0.02, represented by the smallest symbol and 0.66 which is represented by the largest symbol. Refer to Figure 2. 2 for sample legend.

The granites and granitic gneisses in the Buffels River catchment typically have elevated wt% K_2O and variable wt% Na_2O and elemental Sr concentrations and lower wt% CaO, with K-feldspar (microcline) being the dominant feldspar (Macey *et al.*, 2018, 2011). Although the granitic gneisses in the Buffels River catchment are dominated by K-feldspar, the increase in K in groundwater hosted in these rocks is not as significant as the increase in Ca. The small increase in concentration and overall, much lower concentration of K can be explained by various processes or the lack thereof. The low precipitation rate in the Buffels River catchment is a limitation to chemical weathering as water facilitates the chemical reactions during this weathering process. This in turn leads to slow soil formation rates which are necessary for K-feldspar weathering and thus the mobilisation of K. To add to this, K is easily trapped in the interlayers of K minerals which are generally the weathering product of granitic rocks (White, Bullen, Schulz, *et al.*, 2001; Worthington, Davies & Alexander, 2016). Thus, the combination of low precipitation rates, slow soil formation rates, the lack of chemical weathering, which is necessary for the mobilisation of K and the entrapment of K in the interlayers of clay minerals, contributes to the low K concentration in the groundwater in the Buffels River catchment. Furthermore, K-feldspar is less soluble than plagioclase or albite and K is less mobile in water than Na which allows for dissolution of plagioclase and mobilisation of Na and Ca within the fractured aquifer matrix whereas K is generally mobilised once soil formation has started (White & Buss, 2013) (Figure 2. 13). Analysis of HCO_3^-/Na vs Ca/Na ratios indicates that groundwater hosted by the granitic gneisses is inclined to ratios that are typically controlled by silicate weathering (Figure 2. 14) (Gaillardet, Dupre, Louvat, *et al.*, 1999).

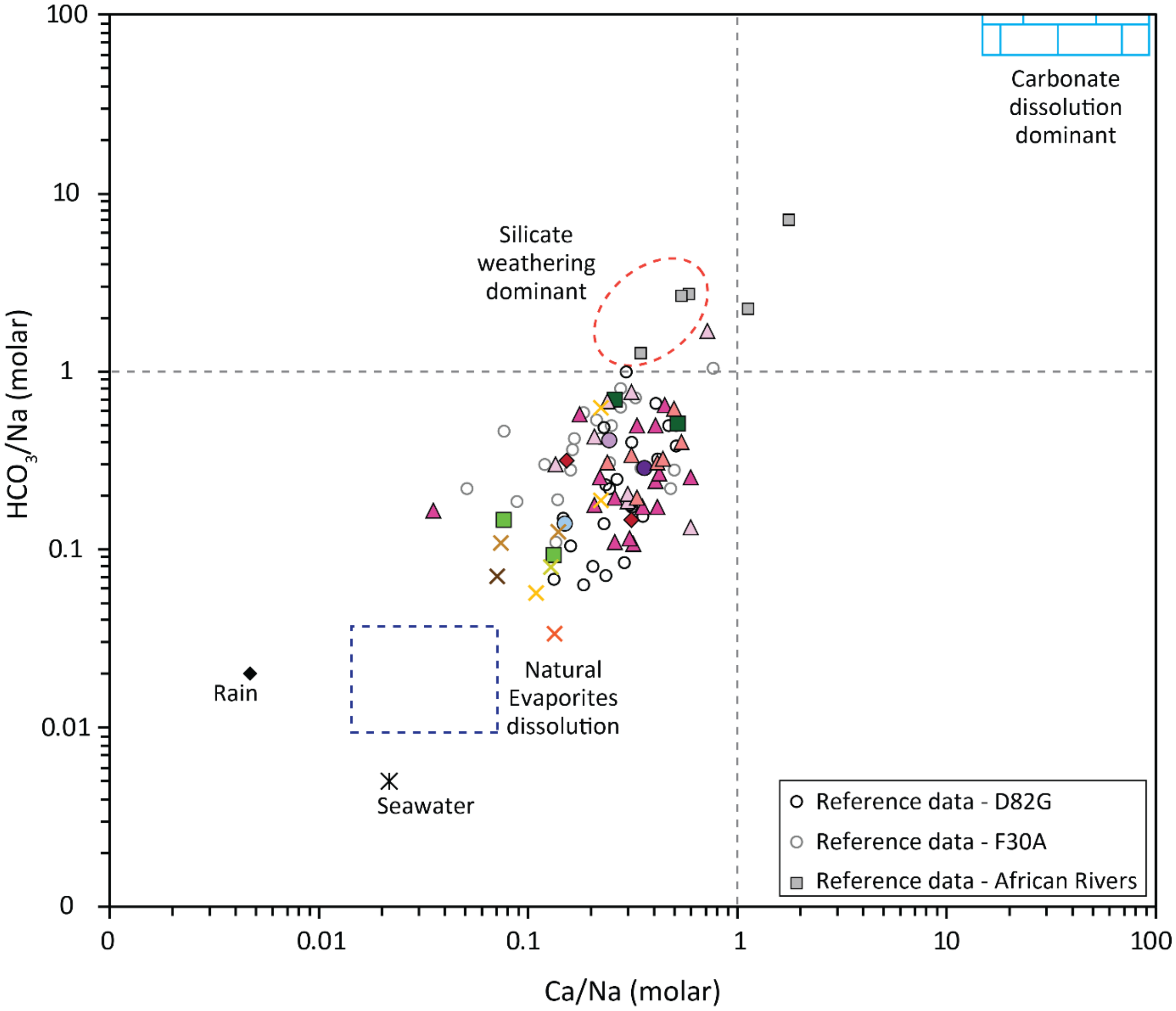

Figure 2. 14: HCO^3/Na ratio vs Ca/Na ratio for groundwater samples collected as well as groundwater reference data from Abiye and Leshomo (2013) and data from African rivers from Gaillardeta et al. (1999). Marked fields indicate the ionic ratios expected as a result of evaporite dissolution, silicate weathering and carbonate dissolution as proposed by Gaillardeta et al. (1999). Refer to Figure 2. 2 for sample legend.

As explained in section 5.2.2 and 5.2.3, the groundwater chemistry in the Buffels River catchment is affected by atmospherically transported marine aerosols and mineral weathering reactions. Salts from dry deposition of marine aerosols are dissolved and transported into soils during precipitation events where ion-exchange reactions occur, and salts present in the soils are also incorporated. From there, potential recharge percolates further down, into the fractured aquifer system where further ion exchange reactions and mineral weathering processes occur along flow paths within the granitic gneiss host rocks. However, whilst these processes contribute to the overall salinisation of the regional groundwater, the data suggests that zones of more intense salinisation can be very localised, and we suggest that this is linked to salts concentrated in heuweltjies.

2.5.3 Linking Heuweltjies to Groundwater Salinity

Several studies have shown that heuweltjies consist of nutrient-rich soils containing increased concentrations of salt-forming ions (Francis *et al.*, 2013; Midgley *et al.*, 2012a; Moore & Picker, 1991b). In nearly all heuweltjie and interheuweltjie pairs sampled in this study, the water-soluble soil EC values on the mound are an order of magnitude higher than for the interheuweltjie soils (Figure 2. 9). This was confirmed by the EM-38 scans which showed a clear difference in the conductivity of soils on and off the heuweltjies (Figure 2. 10). Groundwater with higher EC levels, was also often located where heuweltjies occur in high densities, such as in the Buffels River valley. Moreover, in the case where heuweltjies were sampled in close proximity to boreholes, the heuweltjie soil EC was comparable to that of the groundwater EC (Figure 2. 9). This suggests that there is a spatial relationship between heuweltjies and groundwater salts. Although the specific composition of the heuweltjie salts has not be quantified in this study and it is not clear why salts are so concentrated in the heuweltjies, the spatial relationship between the heuweltjies and saline groundwater presents the possibility that groundwater salts may be linked to salts stored in heuweltjies. Therefore, given a viable pathway and mechanism, transfer of the water-soluble salts in the heuweltjie, would generate elevated groundwater salinities. Although heuweltjies are shallow domes on the surface, suggesting preferential runoff during episodic precipitation events, the centre of the dome is often exploited by large and small burrowing animals including termites, and these burrows could act as preferential flow paths that could extend down to the groundwater system (McAuliffe et al., 2019). Further evidence for penetration of rainfall into the centre of heuweltjies is that the calcite in heuweltjies in the region have been affected by repeated dissolution-re-precipitation (Francis & Poch, 2019). Thus, all that is necessary to transfer heuweltjie salts to the groundwater system is a sufficient volume of water to flush the salts.

2.5.4 Hydrological Patterns and Salt Flushing

In arid and semi-arid regions, episodic precipitation events are the mechanism by which salts that have accumulated on the surface and in the soil horizons, are flushed down into the groundwater system. Although this process can lead to increased salt loads in the groundwater system, it is also an important process for moving salts through the system and preventing their build up. In particular, for this area, Benito et al. (2011) has postulated that episodic flooding of the Buffels River is an important mechanism by which salts are flushed out of the shallow Spektakel Aquifer and the aquifer re-saturated with fresher water. The same process would be necessary for moving heuweltjie salts to the groundwater system. Rainfall records from the past 150 years from the town of Springbok, located around the middle of the catchment, show no clear evidence for changes in the amount and frequency of precipitation events (Davis *et al.*, 2016). However, the data does show multiple high-volume rainfall events, defined as rainfall of more than 40 mm per event, with all rain events of more than 100 mm per event occurring in the last 30 years. Thus, in the past 150 years there have been multiple events sufficient for flushing of salts to occur during recharge. Given that heuweltjies could be up to 30 000 years old (Midgley *et al.*, 2002; Potts *et al.*, 2009) and that there have been many periods in the past 100 000 years where Namaqualand has seen wetter climatic conditions (Dewar & Stewart, 2016), this process of flushing of heuweltjie salts into the groundwater system might have been an ongoing process for thousands of years.

2.5.5 Economic Implications and the Effect on Development.

Groundwater salinity has a direct impact on the local economy, which is dominated by agriculture, as well as the livelihoods of the local communities who rely wholly on groundwater. The main agricultural activity in the Buffels River catchment is pastoralism. Historically, livestock were kept in large fenced-off “camps” to graze on natural vegetation and minimum supplementary feed was required. However, in recent years, increased periods of drought resulted in minimal growth of natural vegetation which forced many farmers to rely on cultivated pastures or crop production for feed, and required increased irrigation pumped from both shallow and deep aquifer systems (Adams *et al.*, 2004; Müller, Igshaan Samuels, Cupido, *et al.*, 2019). To successfully develop pastures, both suitable agricultural land as well as a sufficient water supply is necessary. Although the Buffels River catchment may have enough agricultural land to develop pastures, this study has shown that the soil quality as well as the groundwater availability and quality may be a concern. Although the density of heuweltjies in the catchment is not quantified at present, the high apparent concentration of heuweltjies seen on satellite imagery in the catchment would cause many difficulties in terms of soil quality, especially if these heuweltjies are to be reworked to cultivate some of the land. Moreover, the variably saline nature of the groundwater could lead to crop damage as well as increased soil and groundwater salinity through irrigation return flows. Although the impact of soil and groundwater salinity could be mitigated by introducing specific salt tolerant crops to the region, allowing new agricultural development possibilities, the apparent link between heuweltjies and saline groundwater could make ongoing management of both soil and groundwater challenging unless this link is better quantified.

2.6 Conclusions

Salinisation of groundwater is a major problem, especially in semi-arid to arid environments where groundwater is often one of the only sources of water. The hydrochemistry and isotopic data from groundwater samples in the Buffels River catchment highlighted that it is difficult to define specific groundwater types that might reflect different aquifer systems or flow paths through the catchment with the groundwater hydrochemistry instead being closely associated with the specific rocks types that the groundwater was abstracted from. Whilst evaporation has been previously postulated as a major control on groundwater salinity, the results from this study indicate that evaporative concentration of salts is not as major a contributor to groundwater salinisation. The main sources of groundwater salts are dry deposition of marine aerosols, ion exchange reactions and mineral weathering. The results of this study also support the contention that heuweltjies are important sources of salt, where salts may have accumulated for thousands of years, and potentially contribute to groundwater salinisation through flushing of salts during intense precipitation events. The origin of heuweltjies is still a matter of debate and it is unclear what mechanism causes concentration of the salts in the cores of heuweltjies although it seems likely that termites play some role. These are critical issues to resolve in order to better understand the biogeochemical linkages between heuweltjies, termite activity and saline groundwater. Whilst such an understanding is critical to the management of saline groundwater in this region to enable economically viable agricultural development possibilities, the results also have important implications for other arid and semi-arid regions around the world where termite activity and poor-quality groundwater co-exist.

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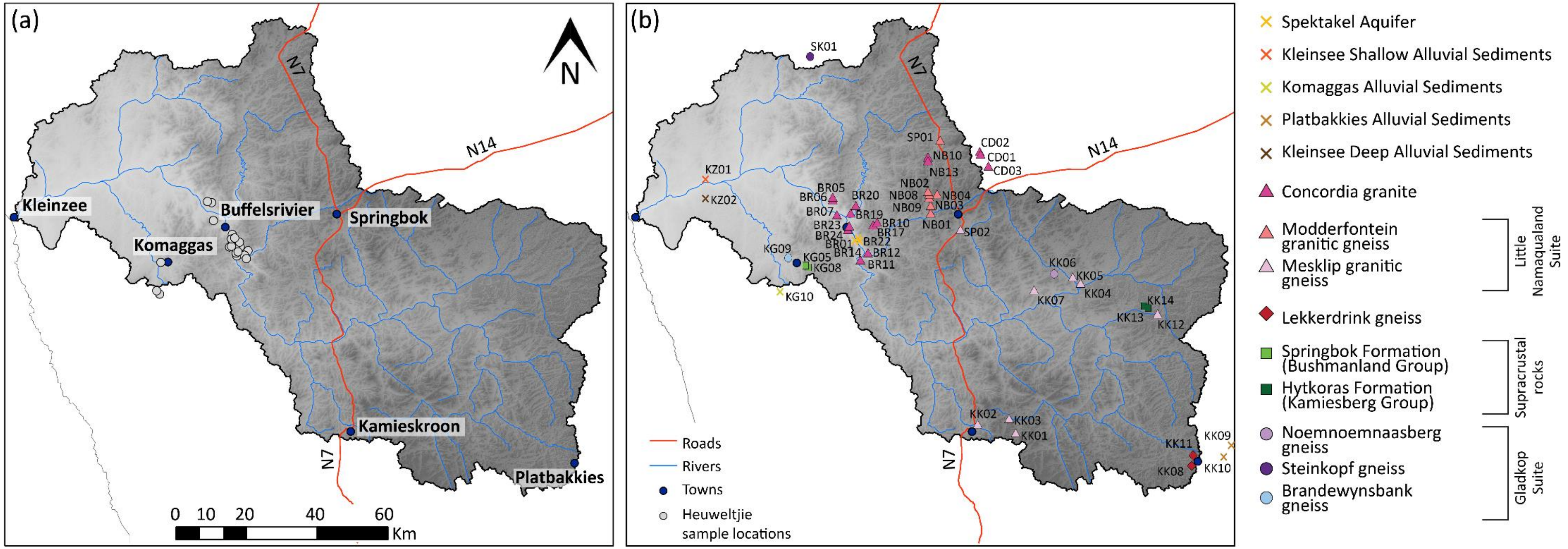
2.8 Supplementary material



Supplementary Figure 2. 1: (a) Sample locations of heuweltjies, (b) groundwater sample locations grouped by colour and symbol in terms of host rock geology.

Supplementary Table 2. 1: Hydrochemical data from groundwater in the Buffels River catchment.

Aquifer Type	**Borehole ID**	**Latitude**	**Longitude**	**EC** **µS/cm**	**pH**	**Na$^+$** **mg/l**	**K$^+$** **mg/l**	**Ca^{2+}** **mg/l**	**Mg^{2+}** **mg/l**	**SO$_4^{2-}$** **mg/l**	**Cl$^-$** **mg/l**	**HCO$_3^-$** **mg/l**	**Sr^{2+}** **µg/l**
Spektakel Aquifer	BR01	-29.73515	17.62710	1828	6.66	167	7.46	64.2	34.7	85.6	393	84.5	
	BR14	-29.73487	17.62887	1314	7.12	126	3.77	24.1	8.74	17.0	438	19.1	
	BR22	-29.73485	17.62921	3129	7.64	227	30.7	88.1	32.1	2.31	503	379.6	
Komaggas Alluvial Sediments	KG10	-29.87144	17.42986	4416	6.8	375	20.5	84.1	82.8	172	1097	80.3	1745
Shallow Kleinsee Alluvial Sediments	KZ01	-29.58434	17.24142	5556	6.78	587	26.9	137	147	212	2034	52.8	
Platbakkies Alluvial Sediments	KK09	-30.26259	18.60989	5349	7.33	626	19.3	150	124	348	1486	207.6	1724
	KK10	-30.29127	18.58695	4651	7.57	806	24.7	103	89.5	307	1414	232.2	1040
Deep Kleinsee Alluvial Sediments	KZ02	-29.63255	17.24051	3184	6.91	350	25.6	43.2	55.6	80.3	914	66.4	445
Concordia Granites	BR06	-29.63531	17.5633	3368	7.18	310	6.92	170	38.2	306	636	88.0	
	BR24	-29.71283	17.60143	1554	7.29	131	3.15	75.1	25.2	60.2	299	171.8	
	BR05	-29.63419	17.56300	2559	7.08	304	6.04	162	29.0	268	592	93.4	3363
	BR10	-29.70188	17.66447	1114	6.58	116	1.80	52.0	24.2	73.0	228	60.3	240
	BR11	-29.79109	17.63366	1736	6.36	170	5.64	61.5	17.9	77.9	374	80.4	
	BR12	-29.76827	17.65701	3379	7.47	286	2.97	130	76.4	246	737	84.3	
	BR17	-29.70621	17.65581	703	7.47	68.8	2.36	54.0	17.7	45.6	123	119	210
	BR19	-29.67026	17.60819	2432	6.64	172	5.17	124	63.6	119	624	78.7	
	BR20	-29.65168	17.62098	1868	6.3	133	2.59	94.7	37.0	113	370	85.5	
	BR23	-29.70553	17.6054	4860	6.93	359	9.50	218	106	215	1000	164	1510
	CD01	-29.52169	17.93939	1144	7.4	131	1.80	39.7	15.7	191	93.5	200	
	BR07	-29.67542	17.57308	1522	6.77	167	1.46	64.2	36.5	98.4	367	111	421
	NB10	-29.53268	17.80581	686	8.73	101	1.88	6.16	2.20	11.1	165	44.5	

Aquifer Type		**Borehole ID**	**Latitude**	**Longitude**	**EC**	**pH**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**SO_4^{2-}**	**Cl^-**	**HCO_3^-**	**Sr^{2+}**
					µS/cm		**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**µg/l**
Little Namaqualand Suite	Concordia Granites	NB13	-29.53205	17.80647	2046	6.7	122	2.57	89.9	48.6	263	369	86.5	
		CD02	-29.51786	17.93852	873	6.75	82.4	1.41	57.7	21.3	163	106	110	463
		CD03	-29.55198	17.96047	2716	6.95	167	2.86	172	102	223	744	112	1560
	Modderfontein Granitic Gneiss	NB01	-29.67259	17.81307	950	6.53	85.9	4.49	49.7	24.4	67.3	215	44.1	563
		NB02	-29.61753	17.80591	622	6.24	52.2	0.81	28.5	13.1	88.8	109	47.4	200
		NB03	-29.65299	17.81244	716	6.33	67.5	2.21	27.9	29.4	79.4	158	54.6	149
		NB04	-29.62262	17.82860	1035	6.55	96.7	1.40	69.7	23.1	186	186	78.7	229
		NB08	-29.62387	17.80944	2202	6.91	144	1.16	109	44.5	369	373	123	
		NB09	-29.63147	17.80986	1676	7.07	116	2.61	101	35.6	154	284	188	
		SP02	-29.71346	17.89191	3347	7.21	154	2.16	144	83.4	453	1198	164	5884
	Mesklip Granitic Gneiss	KK02	-30.21011	17.93390	613	6.48	56	0.93	23.3	25.3	40.7	111	101	159
		KK05	-29.83037	18.17545	1342	6.82	126	1.06	65.7	29.6	100	314	62.9	298
		KK07	-29.87172	18.08016	1888	6.88	193	4.60	69.0	34.2	149	400	219	407
		KK01	-30.23190	18.02912	231	6.55	28.9	0.90	6.77	5.12	7.74	37.2	23.0	46
		KK03	-30.19694	18.01319	388	7.29	27.0	0.74	33.9	8.88	2.46	10.8	121	154
		KK04	-29.84888	18.19154	1468	7.06	140	2.61	72.2	31.6	109	367	76.1	362
		KK12	-29.92465	18.39290	854	7.18	64.1	0.96	34.8	32.1	37.0	140	129	221
		SP01	-29.48521	17.83574	4362	7.07	329	6.71	340	88.3	145	574	117	1586
	Lekkerdrink Gneiss	KK08	-30.31133	18.47991	5465	7.25	451	17.78	241	168	305	1809	176	2202
		KK11	-30.28448	18.48435	2286	7.46	258	9.62	68.3	31.4	155	480	214	503
Supracrustal rocks	Bushmanland Group	KG05	-29.79890	17.492802	1089	6.36	110	7.07	25.8	45.1	78.2	297	26.7	
		KG08	-29.80213	17.49838	761	6.3	92.1	5.06	12.6	24.1	28.3	220	35.0	130
	Kamiesberg Group	KK13	-29.91084	18.36609	3093	6.86	208	3.70	190	144	329	709	276	1103
		KK14	-29.91019	18.36615	1316	7.57	132	2.64	60.2	41.0	101	223	235	285

Aquifer Type		**Borehole ID**	**Latitude**	**Longitude**	**EC**	**pH**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**SO_4^{2-}**	**Cl^-**	**HCO_3^-**	**Sr^{2+}**
					µS/cm		**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**µg/l**
Supracrustal rocks	Kamiesberg Group	KK13	-29.91084	18.36609	3093	6.86	208	3.70	190	144	329	709	276	1103
		KK14	-29.91019	18.36615	1316	7.57	132	2.64	60.2	41.0	101	223	235	285
Gladkop Suite	Brandewynsbank Gneiss	KG09	-29.77891	17.45266	3077	6.85	252	14.43	66.4	72.4	140	715	92.2	
	Noemnoemnaasberg Gneiss	KK06	-29.82022	18.13321	1832	6.88	168	2.43	71.9	35.8	126	342	177	371
	Steinkopf Gneiss	SK01	-29.26940	17.51072	2330	7.4	187	6.07	119	59.4	280	795	140	748

Supplementary Table 2. 2: Isotopic data from the groundwater in the Buffels River catchment.

Aquifer Type		**Borehole ID**	**δ^{2}H ‰**	**δ^{18}O ‰**	**d-excess**	**^{87}Sr/^{86}Sr**
	Spektakel Aquifer	BR22	-13.7	-3.27	12.5	
		BR01	-21.9	-4.03	10.3	
		BR14	-15.6	-3.47	12.2	
	Komaggas Alluvial Sediments	KG10	-12.3	-2.51	7.86	
	Shallow Kleinsee Alluvial Sediments	KZ01	-14.4	-2.88	8.63	0.71997
	Platbakkies Alluvial Sediments	KK09	-32.8	-4.09	-0.14	0.71902
		KK10	-32.1	-4.10	0.69	0.71861
	Deep Kleinsee Alluvial Sediments	KZ02	-14.0	-2.87	8.96	0.71355
	Concordia Granites	BR06	-15.1	-3.01	8.93	
		BR24	-13.2	-2.47	6.59	
		BR05	-16.1	-3.15	9.07	0.73625
		BR10	-13.6	-3.12	11.4	0.76232
		BR11	-18.1	-3.85	12.7	
		BR12	-17.1	-3.44	10.4	
		BR17	-16.9	-4.02	15.3	0.75748
		BR19	-13.7	-2.67	7.62	0.74645
		BR20	-14.6	-3.39	12.6	
		BR23	-14.7	-2.50	5.30	0.74835
		CD01	-18.4	-3.76	11.6	
		BR07	-11.7	-2.74	10.2	0.74689
		NB10	-17.2	-3.97	14.5	
		NB13	-19.1	-3.83	11.5	
		CD02	-19.6	-4.01	12.4	0.73734
		CD03	-22.4	-3.45	5.24	0.75174
Little Namaqualand Suite	Modderfontein Granitic Gneiss	NB01	-23.3	-4.46	12.4	0.73117
		NB02	-13.4	-3.17	12.0	0.74344
		NB03	-23.2	-4.55	13.2	0.74248
		NB04	-21.3	-4.47	14.5	0.74670
		NB08	-17.5	-3.24	8.45	
		NB09	-24.5	-4.59	12.2	
		SP02	-22.3	-3.93	9.07	0.73899

Aquifer Type		**Borehole ID**	**δ^{2}H ‰**	**δ^{18}O ‰**	**d-excess**	**^{87}Sr/^{86}Sr**
Little Namaqualand Suite	Mesklip Granitic Gneiss	KK02	-17.1	-3.32	9.46	0.72381
		KK05	-30.6	-5.25	11.4	0.75681
		KK07	-31.9	-4.52	4.29	0.73085
		KK01	-17.5	-3.24	8.44	0.75657
		KK03	-23.6	-4.80	14.8	0.76934
		KK04	-31.1	-5.17	10.2	0.75077
		KK12	-27.6	-4.13	5.41	0.72588
		SP01	-24.8	-4.62	12.2	0.71749
	Lekkerdrink Gneiss	KK08	-33.9	-4.56	2.59	0.72243
		KK11	-31.4	-4.94	8.08	0.72325
Supracrustal rocks	Bushmanland Group	KG05	-15.9	-3.74	14.1	0.74814
		KG08	-15.7	-3.75	14.3	0.74338
	Kamiesberg Group	KK13	-31.9	-5.08	8.74	0.73113
		KK14	-30.5	-4.81	8.04	0.72915
Gladkop Suite	Brandewynsbank Gneiss	KG09	-13.5	-2.82	9.10	
	Noemnoemnaasberg Gneiss	KK06	-32.5	-5.25	9.49	0.75332
	Steinkopf Gneiss	SK01	-19.3	-3.57	9.27	0.73482

Supplementary Table 2. 3: Water-soluble EC values for heuweltjie soils in the Buffels River catchment.

Sample ID	**Latitude**	**Longitude**	**Description**	**EC (µS/cm)**	**Minimum (µS/cm)**	**Maximum (µS/cm)**	**Mean EC (µS/cm)**	**1s St Dev (µS/cm)**
BRH01	-29.76908	17.63736	Heuweltjie	3548	888	6124	3315	2003
			Interheuweltjie	888	76.4	304	133	75.1
BRH02	-29.74619	17.63054	Heuweltjie	297	144	3755	2163	1604
			Interheuweltjie	2534	15.0	123	49.4	46.2
BRH03	-29.73929	17.62589	Heuweltjie	172	119	172	145	26.7
			Interheuweltjie	119	14.6	839	183	278
BRH04	-29.74413	17.63879	Heuweltjie	1713	568	3877	1822	1370
			Interheuweltjie	3097	13.6	135	69.7	40.3
BRH05	-29.74431	17.63929	Heuweltjie	7464	235	7464	4107	2972
			Interheuweltjie	4596	15.7	107	52.5	33.2
BRH06	-29.77358	17.64739	Heuweltjie	1718	127	6242	3149	2520
			Interheuweltjie	6242	17.2	129	81.9	35.9
BRH07	-29.77225	17.65132	Heuweltjie	2827	226	5259	2253	1980
			Interheuweltjie	5259	17.8	546	159	179
BRH08	-29.6794	17.57301	Heuweltjie	1108	250	1217	771	414
			Interheuweltjie	1089	123	201	170	34.7
BRH09	-29.68001	17.57204	Heuweltjie	205	19.2	3400	633	1357
			Interheuweltjie	101	16.6	16.6	16.6	-
BRH10	-29.63304	17.55955	Heuweltjie	5119	2738	6907	5465	1378
			Interheuweltjie	5661	128	2247	762	1003
BRH11	-29.63511	17.56391	Heuweltjie	131	12.0	250	162	85
			Interheuweltjie	250	9.79	11.0	10.5	0.55
BRH12	-29.77266	17.65286	Heuweltjie	12479	593	12479	5335	2414
			Interheuweltjie	6162	17.1	102	71.0	37.0
BRH13	-29.7646	17.65297	Heuweltjie	2989	136	5422	2517	1951
			Interheuweltjie	3443	11.6	65.8	24.5	20.4
BRH14	-29.76628	17.65534	Heuweltjie	85.6	76.2	1901	471	606
			Interheuweltjie	1901	11.9	141	36.2	51.2
BRH15	-29.76654	17.63662	Heuweltjie	2536	236	13122	5967	4561
			Interheuweltjie	10986	107	181	133	34.3
BRH16	-29.76782	17.64031	Heuweltjie	12720	280	14989	8036	6027
			Interheuweltjie	12308	128	685	276	235
BRH17	-29.77147	17.63774	Heuweltjie	15565	258	15565	5767	5069
			Interheuweltjie	7978	109	8298	3031	3995
BRH18	-29.76268	17.63969	Heuweltjie	329	329	6420	2998	2124
			Interheuweltjie	2726	14.9	327	90.3	135
KGH03	-29.85774	17.42588	Heuweltjie	784	180	2104	700	639
			Interheuweltjie	2104	11.1	397	177	162
KGH04	-29.87061	17.435774	Heuweltjie	187	187	4283	1603	1284
			Interheuweltjie	2312	16.0	1270	327	536
KGH05	-29.87057	17.43558	Heuweltjie	11.7	4.33	3702	1601	1129
			Interheuweltjie	128	102	1120	380	388

CHAPTER 3.

PAPER PUBLICATION HISTORY	
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Impact of residence time constraints on groundwater sustainability and implications for agricultural development: A case study from the Buffels River catchment, Northern Cape, South Africa.

J van Gend[1], L. Palcsu[2], M. Molnár[2], A. Watson[1], J.D. van Rooyen[1], M.L. Francis[3], C.E. Clarke[3], J.A. Miller[1]*

1. *Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, South Africa*
2. *Isotope Climatology and Environmental Research Centre, Debrecen, Hungary.*
3. *Soil Science Department, Stellenbosch University, Private Bag, X1, Matieland, South Africa*

* Corresponding Author: E-mail address: jmiller@sun.ac.za.

Keywords: Conceptual recharge model, Residence times, Heuweltjies

Abstract

Salinisation of groundwater is a common natural process occurring across many climatic regions. However, deterioration of groundwater quality in a region where many communities are wholly dependent on groundwater as their only source of potable water, further salinisation may be detrimental to the social and economic development in the region. In this contribution, the sustainability of groundwater in the Buffels River catchment in South Africa is investigated in terms of quality and quantity. Conventional radiocarbon age dating methods are evaluated and compared but variable groundwater $\delta^{13}C$ values together with unknowns regarding flow paths resulted in uncertainties regarding the validity of conventional methods and the resultant groundwater ages. After assessing the possible groundwater flow paths which includes saline heuweltjies as preferential flow paths, total mean groundwater ages were calculated via lumped parameter models using tritium and radiocarbon activities in the groundwater. Groundwater in the Buffels River catchment range between modern and fossil, but most of the samples were older than 300 years. Although modern recharge is occurring, the percentage modern recharge remains little. In terms of salinisation of groundwater in the Buffels River catchment, the process does not involve a continuous build-up of salts within the groundwater. The sustainability of groundwater in the Buffels River catchment remains a concern. With climate change predictions, the demand for groundwater in this region is likely to increase, while more salinisation events are expected as the rainfall events will become erratic and intense.

3.1. Introduction

Sub-Saharan Africa has been identified as a region vulnerable to the impacts of climate change because of its dependence on agriculture and limited surface water resources (Fjelde & von Uexkull, 2012; Kotir, 2011; Thornton *et al.*, 2008; WWAP - UNESCO World Water Assessment Programme, 2019). In this region, it is estimated that up to 70% of the population depends on agriculture as a main source of income, with agriculture contributing up to 50 % of the region's GDP (Connolly-Boutin & Smit, 2016; Sheffield *et al.*, 2014). Although rain-fed agriculture is still the dominant component of the sector, there has been an increase in the use of groundwater for irrigation for both commercial and subsistence agriculture in the past decade (Döring, 2020; Villholth, 2013). The move toward increased groundwater use is linked to changes in population growth and urbanisation, as well as precipitation patterns that marginalise established agricultural regions (WWAP - UNESCO World Water Assessment Programme, 2019). Moreover, the population of sub-Saharan Africa is expected to increase by 45% in the next 30 years and this will drive significant demand for food, potable water for human consumption and fresh water specifically in the agricultural sector (Gerten, Heinke, Hoff, *et al.*, 2011; Ojeda Olivares, Belmonte Jiménez, Sandoval Torres, *et al.*, 2020; UNDESA - United Nations, Department of Economic and Social Affairs, 2017). Taken as a whole, these changes will lead to significant pressure on groundwater resources and challenge the sustainability of many aquifer systems (Cobbing & Hiller, 2019; Cooper, Dimes, Rao, *et al.*, 2008; Dore, 2005; World Bank, 2018).

Groundwater sustainability is influenced by both quality and quantity (van Rooyen *et al.*, 2020; Villholth, 2013). In arid and semi-arid regions, salinisation of groundwater is one of the main challenges with regards to groundwater quality (Rengasamy, 2006; Salama, Otto & Fitzpatrick, 1999; van Weert *et al.*, 2009; Yue, Meng, Hou, *et al.*, 2020). Groundwater salinisation can be caused by both natural and anthropogenic processes (Foster & Chilton, 2003; Rengasamy, 2006; Salama *et al.*, 1999) but both have a net negative impact on agricultural productivity. Increasing temperatures and decreasing precipitation in many arid and semi-arid regions of sub-Saharan Africa linked to climate change, are likely to exacerbate the effects of salinisation (Jones & van Vliet, 2018; Taylor, Koussis & Tindimuguya, 2009; Van Vliet, Florke & Wada, 2017). Recent developments in water treatment technology though now mean that it is more affordable and accessible to treat saline or poor-quality groundwater by various processes, including nano-filtration and reverse osmosis, depending on the needs of the community (Greenlee, Lawler, Freeman, *et al.*, 2009; Lew, Tarnapolski, Afgin, *et al.*, 2019). However, the effect of changing precipitation patterns on groundwater availability and the quantity or volume thereof is challenging to evaluate and address. Decreased precipitation in areas where groundwater resources are already under pressure will leave both communities and eco-systems vulnerable to the impacts of climate change (Botai, Botai & Adeola, 2018; Edmunds, 2009; Taylor *et al.*, 2009).

Assessment of groundwater quantity is dependent on a number of factors including the renewal rate of the groundwater system. However, to understand the renewal rate, an understanding of the groundwater residence time is also required to evaluate the timescales over which the stored groundwater is being turned over. Recently, it has been proposed to divide groundwater into three broad categories based on residence time. Under this grouping, fossil groundwater is represented by groundwater that was recharged before 12 ka, while modern groundwater is represented by groundwater that was recharged less than 50 years ago (Bierkens & Wada, 2019; Gleeson, Befus, Jasechko, *et al.*, 2016; Jasechko *et al.*, 2017). Groundwater that has been recharged between 12 ka and 50 years ago would be referred to as young groundwater (Bierkens & Wada, 2019; Margat, Foster & Droubi, 2006). Methods used to differentiate fossil, young and modern groundwaters include using longer-lived radio-isotopes such as radiocarbon (half-life of 5700 years) for fossil and young groundwaters and short lived radio-isotopes such as tritium (half-life of 12.312 years) for modern groundwaters (Cartwright, Cendón, Currell, *et al.*, 2017; Cartwright, Currell, Cendón, *et al.*, 2020; Jasechko *et al.*, 2017; Meredith, 2009; Newman, Osenbrück, Aeschbach-Hertig, *et al.*, 2010). Considering the half-lives of these two isotopes, fossil or young groundwater should not contain any tritium as this would indicate modern recharge. However, detectable levels of tritium are often present in fossil groundwater suggesting that the supposed isolation of fossil groundwater from the modern groundwater system or modern precipitation may not be valid (Jasechko *et al.*, 2017). Not only does this indicate mixing between old and modern groundwater, but it also indicates that fossil or young groundwater is more susceptible to surface water - groundwater interaction than previously thought (Jasechko *et al.*, 2017; Tweed *et al.*, 2018).

Residence times of groundwater in this region have been previously estimated using ^{14}C and the conventional decay equation but a wide range of ^{14}C activities were found, ranging between 1.6 and 120 pMC with associated ages of 32,000 years to modern (Adams *et al.*, 2004). These ages did not show any significant spatial relationships and some of the age data did not agree with the recharge model that was used during this study. However, many of the samples analysed had detectable levels of tritium irrespective of the low ^{14}C activity (Adams *et al.*, 2004), indicating interaction between fossil or young waters and modern waters. Given the dependence on the groundwater system in this region, properly constraining the residence time spectrum is necessary to better understand the potential mixing relationships between fossil and modern groundwater.

In this study, the sustainability of groundwater in the Buffels River catchment in Namaqualand on the west coast of South Africa was evaluated by using ^{14}C, ^{3}H and $\delta^{13}C$ as tracers of groundwater residence time and flow. In order to do this, the recharge mechanisms for different aquifers in the different areas within the catchment were conceptualised to better understand how precipitation is transferred to the groundwater system. Then, conventional radiocarbon age calculations on dissolved inorganic carbon (DIC) in the groundwater were evaluated and $\delta^{13}C_{DIC}$ values were used to investigate the possibility of dilution of the groundwater ^{14}C. Finally, a lumped parameter model approach (LPM), was used to calculate total mean ages and identify mixing relationships between older and younger groundwaters. The results of this study highlight the complexity of the groundwater system in the region and the challenges the area faces with developing a robust groundwater management strategy. However, understanding these complexities in semi-arid and arid environments, that heavily rely on agriculture, is essential to the development of strategies to address climate change and understand hydrological resilience throughout much of sub-Saharan Africa.

3.2. Environmental Setting

The Buffels River is the largest ephemeral river in Namaqualand with a catchment of 9250 km^{2} (Figure 3. 1). Its headwaters are situated in the Kamies Mountains on the Bushmanland Plateau at an elevation of approximately 1500 m a.m.s.l. From there, the river cuts down into the escarpment and subsequently onto the Tertiary coastal plain approximately 40 km from the coast thereafter entering the Atlantic Ocean at the town of Kleinsee (Benito *et al.*, 2010; Benito, Thorndycraft, *et al.*, 2011; Marais *et al.*, 2001a). The catchment forms part of a global diversity hot-spot hosting seven bioregions, including ~25% of the Succulent Karoo biome (Desmet, 2007; Rutherford, Mucina & Powrie, 2006).

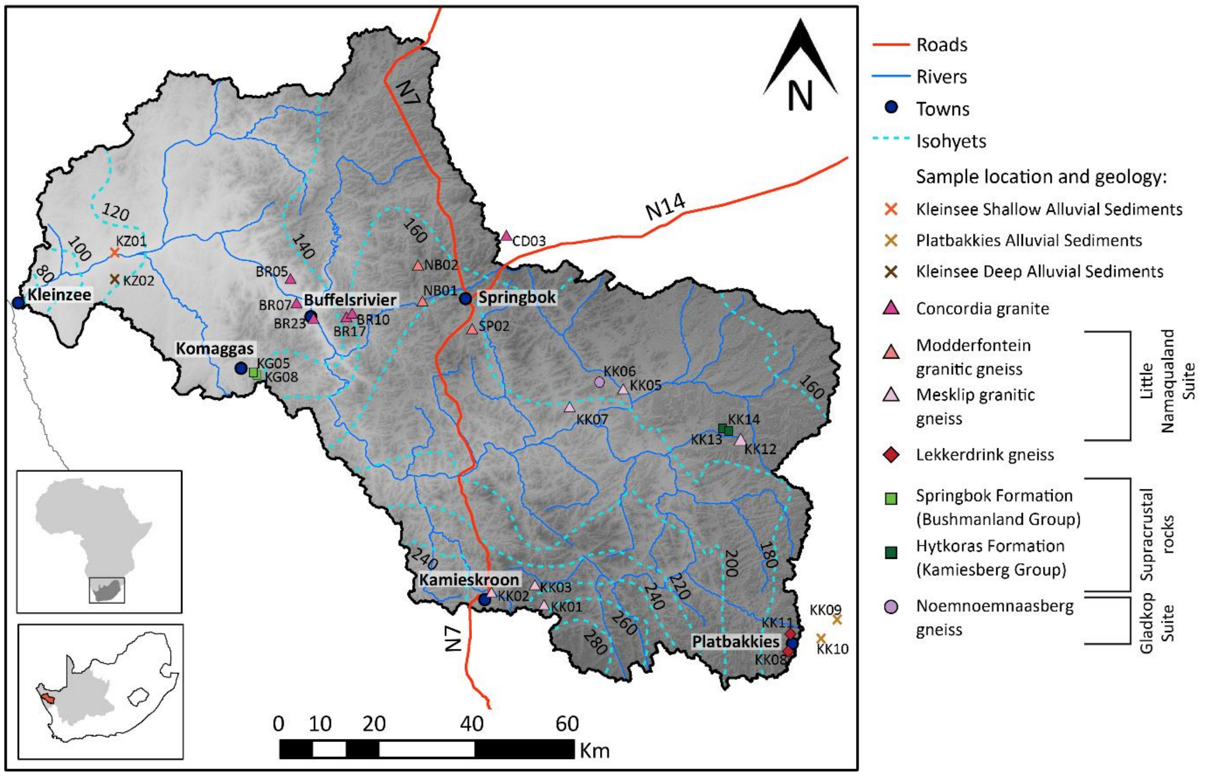

Figure 3. 1: Location of the Buffels River catchment in South Africa with the river tributaries, isohyets and sample locations indicated on the map. The different symbol used to show sample locations refers to the host rock geology.

3.2.1. Climate

Namaqualand has a semi-arid to hyper-arid climate with a mean annual precipitation of 450 mm per year in the Kamies Mountains decreasing to 110 mm per year on the coastal plain, while the mean annual precipitation at the coast is 50 mm per year (Benito, Botero, Thorndycraft, *et al.*, 2011; Pietersen *et al.*, 2009; Titus *et al.*, 2009). Most of the Buffels River catchment falls within the winter rainfall area where precipitation is linked to frontal systems off the Atlantic Ocean (Benito, Botero, *et al.*, 2011; Davis *et al.*, 2016). Temperatures in the region are variable, with temperatures up to 40 °C in the day during hot dry summers and frequent sub-zero temperatures overnight during winter (SAWB, 2013). Fog (summer months) and dewfalls (mid-winter) contribute significantly to surface moisture along the coastal zone of this catchment. Coastal fog frequency in Namaqualand is about 75 fog days per year, decreasing towards the east or inland (Davis *et al.*, 2016; Olivier, 2002). However, it has been predicted that climate change will not only cause a decrease precipitation in the region but also a reduction in coastal fog formation as a result of increasing sea surface temperature (Beal, De Ruijter, Biastoch, *et al.*, 2011; Biastoch, Böning, Schwarzkopf, *et al.*, 2009; Weldeab *et al.*, 2013).

3.2.2. Vegetation

The flora in Namaqualand is known to be drought resistant with leaves and roots adapted for the arid climatic conditions (Mucina & Rutherford, 2006). Although the vegetation in this region is sparse, the dominant vegetation throughout western Namaqualand is Succulent Karoo biome, generally consisting of shallow rooted drought resistant leaf-succulents, which are C3 plants. Towards the east of the catchment, the Succulent Karoo biome co-exists with the Nama Karoo biome. Although the Nama Karoo biome is also dominated by C3 species, the presence of C4 grass species increase towards the east where they co-exist with C3 low shrubs of the Nama Karoo biome. (Carrick & Krüger, 2007; Mucina & Rutherford, 2006). Sparse Acacia Karoo shrubs and thicket species, which are mostly C3 species, only exist in the alluvial plains of the Buffels Rive due to their dependence on groundwater. During periods of severe drought these riparian plant species typically do not survive.

3.2.3. Geomorphology

The geomorphology of the Buffels River catchment can be divided into three zones: 1) the western coastal lowland or plain, characterised by crystalline basement rocks overlain by younger sedimentary rocks and sands; 2) the Namaqualand highlands or escarpment zone comprised of exposed granitic domes, interspersed with thick layers of weathered material cut by alluvial paleochannels. The granitic domes, also known as Bornhardts, are often separated by valleys and narrow plains and are typical of the geomorphology of Namaqualand. They host extensive orthogonal fracture systems that can be linked to groundwater flow paths (Twidale, 2007) and ; 3) the gently undulating Bushmanland Plateau occurring at higher elevation towards the east of the catchment and consisting of a complex sequence of erosional and aggradational phases (Adams *et al.*, 2004; Titus *et al.*, 2009) .

Prominent biophysical features that occur on all three geomorphological zones are heuweltjies. Heuweltjies are large but shallow mounds particularly concentrated throughout the Buffels River catchment and on the coastal plain towards Kleinsee. These features consist of aerated and nutrient-rich soils (Francis *et al.*, 2013; Kunz *et al.*, 2012; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Midgley & Musil, 1990; Midgley *et al.*, 2012a) and are generally up to 30 m in diameter and up to 3 m high although diameters of up to 50m have been observed in the Buffels River valley. Although the formation of heuweltjies is still a matter of considerable debate, it seems likely that heuweltjies are linked to the termite Microhodotermes *viator*, (Cramer *et al.*, 2017; Cramer & Midgley, 2015; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Timm Hoffman, Mcfadden, *et al.*, 2014; Midgley *et al.*, 2002) and excavated heuweltjies have shown complex networks of termite and other species burrowing within the heuweltjie at a variety of scales (Vermooten, 2019). These tunnels and aerated bioturbated soils could potentially act as preferential flow paths to facilitate recharge and it has been shown that the salinity in heuweltjies increase with depth (van Gend, Francis, Watson, *et al.*, 2020), suggesting that salts are transported downwards through the heuweltjie. Heuweltjies cover up to 25% of the overall land surface in western South Africa (Lovegrove & Siegfried, 1989). Given that in the Buffels River catchment, this equates to approximately 2313 km^2, heuweltjies may play a large role in groundwater recharge and possibly salinisation of groundwater.

3.2.4. Geological Context

Geologically, Namaqualand and hence the Buffels River catchment, forms part of the Namaqua sector of the Namaqua-Natal Metamorphic Province (Chapter 2, Figure 2. 2). The area is dominated by high-grade granites and gneisses as well as meta-sedimentary and meta-volcanic supracrustal rocks of the Bushmanland Sub-Province (BSP) (Clifford et al., 2004; Eglington, 2006; Cornell et al., 2006; Thomas et al., 2016; Macey et al., 2017a, 2017b). The granitic gneisses of the Gladkop Suite are the oldest rocks in the catchment and have been dated at 1.83 Ga (Robb, Armstrong & Waters, 1999). The Little Namaqualand Suite (1.21-1.19 Ga) consisting of the granitic Modderfontein and Mesklip Gneisses makes up the largest part of the catchment. The suite occurs with the Concordia Granite (1.17 Ga) and granitic Spektakel Suite (1.10-1.03 Ga) in the central part of the catchment and with the Lekkerdrink Gneiss (1.2 Ga) in the southern part of the catchment (Chapter 2, Figure 2. 2) (Clifford, Barton, Stern, *et al.*, 2004; Macey *et al.*, 2018; Robb *et al.*, 1999). The supracrustal rocks of the Kamiesberg Group (1.60 Ga) and the Bushmanland Group (1.15 Ga) occur between the granitic gneisses of the Little Namaqualand Suite (Cornell, Petterson, Whitehouse, *et al.*, 2009; Raith, Cornell, Frimmel, *et al.*, 2003). In the south of the catchment, in close proximity to Leliefontein, fine-grained meta-carbonates occur as part of the Kamiesberg Group (Chapter 2, Figure 2. 2) (Macey *et al.*, 2011). The granitic gneisses as well as supracrustal rocks in the catchment are overlain by various sedimentary successions. Along the coast, sediments rich in quartz, feldspar and phosphatic shell fragments were deposited during cycles of Tertiary sea-level regression, forming part of the regolith (Pether et al., 2000; Roberts et al., 2006). Aeolian sediment accumulation has occurred all over the catchment since the late Quaternary, specifically in the last 100 Ka (Roberts *et al.*, 2014, 2009). The oldest of the aeolian sediments are the red sands stretching furthest inland on the coastal plain (Francis, Fey, Prinsloo, *et al.*, 2007).

3.2.5. Hydrological setting and groundwater quality

Groundwater in the Buffels River catchment is hosted in alluvial and fractured rock aquifer systems. The Spektakel and Kleinsee aquifers are the two known and significant alluvial aquifers in the catchment but there are a number of smaller alluvial aquifers in the catchment that are important water resources in the area. The town of Buffelsrivier, which is situated in the Buffels River valley, is dependent on the Spektakel aquifer for its water supply (Benito, Botero, *et al.*, 2011; Benito, Thorndycraft, *et al.*, 2011; Marais *et al.*, 2001a). The Kleinsee aquifer is situated at the mouth of the Buffels River, where the town of Kleinsee is located. It supports the Buffels River estuary and is protected from the Atlantic Ocean by a sand berm (Massie & Hutchings, 2018). The alluvial aquifers are closely interlinked with the deeper fractured bedrock aquifer systems via weathered zones that serve as pathways for subsurface intergranular flow from the shallow alluvial aquifers to the deeper granitic, gneissic and bedrock aquifers (Benito, Thorndycraft, *et al.*, 2011; Marais *et al.*, 2001a). Groundwater in the deeper fractured aquifer system is mainly hosted in the granitic gneisses and supracrustal rocks of the BSP that are associated with low primary porosity. Groundwater is therefore likely to be hosted in fractures and joint planes, that are variably interconnected and to some extent dependent on the degree of weathering. The hydrochemistry of the groundwater in the Buffels River catchment is largely dependent on the rock type of the aquifer host and clear differences have been noted in the hydrochemistry as well as $^{87}Sr/^{86}Sr$ isotope signatures of groundwater hosted in different rocks in different parts of the catchment (van Gend *et al.*, 2020). Apart from this, the groundwater in the catchment is variably saline which has been ascribed to salt contributions from marine aerosols, mineral weathering and flushing of salts present in the saline soils of heuweltjies rather than evaporative concentration of salts as previously thought (van Gend *et al.*, 2020).

3.3. Methods and Materials

3.3.1. Sample collection / field methods

A total of 34 groundwater samples were collected between March and September 2018 from boreholes, springs, and wells. The hydrochemistry (including alkalinity), $\delta^{18}O$, $\delta^{2}H$ and $^{87}Sr/^{86}Sr$ data of these samples has been previously reported in van Gend et al., (2020). In this contribution, $\delta^{13}C$ ratios as well as the radioactive isotopes of ^{3}H and ^{14}C are presented, and the residence times and mixing relationships are evaluated based on this data. The infrastructure and the pumping regimes of the boreholes in the Buffels River catchment are highly variable. Therefore, all boreholes were purged until EC values stabilised before sampling radioactive tracers. Purging was done via installed submersible pumps. EC and pH in the field were measured using Extech EC600 portable field probes at the point of discharge. ^3H, $\delta^{13}C$ and ^{14}C samples were collected in 500ml high density PP amber bottles directly from the discharge point. All bottles were rinsed 3 times with the groundwater before the final sample was taken. The final sample was taken by allowing the sample bottles to overfill several times to minimize atmospheric CO_2 contamination before it was closed and sealed tightly with the closure additionally taped for added protection. All samples were kept refrigerated at 4°C with minimum light exposure until analysis.

3.3.2. *Sample preparation and analytical techniques*

3.3.2.1. *Tritium*

Tritium was analysed at the Isotope Climatology and Environmental Research Centre (ICER), Debrecen, Hungary via the ^3He ingrowth method with ^4He isotope dilution (Palcsu, Major, Köllő, *et al.*, 2010; Papp, Palcsu, Major, *et al.*, 2012). The process can be simplified to four steps; (1) distillation of water samples, (2) removal of all dissolved gasses through vacuum pumping, (3) storage of samples in stainless steel vessels for several months during which tritium decay occurs, producing ^3He atoms, and (4) measurement of ^3He through admitting the helium fraction that was produced to the dual collector noble gas mass spectrometer (Helix SFT). The tritium concentration was calculated using the abundance of tritogenic helium isotopes. The average analytical uncertainty recorded during analysis of tritium was 0.072 TU.

3.3.2.2. *$\delta^{13}C$ and Radiocarbon*

$\delta^{13}C$ values were determined using a Delta^{PLUS} XP isotope ratio mass spectrometer equipped with a Gasbench-II at ICER. During sample preparation, groundwater samples were placed in a separatory funnel with NaOH. $BaCl_2$ was added to form a cloudy solution, which includes a mixture of $BaCO_3$ and $BaSO_4$, and set aside for the precipitate to accumulate at the base of funnel. The wet precipitate was extracted and washed with ultra-pure water until a neutral pH was reached. Contact with atmosphere was kept to a minimum throughout the process. Samples were freeze dried after which 1 mg of the sample was placed in the GasBench II equipment to continue the process in a closed system. Phosphoric acid was added to the dried precipitate and the released CO_2 was carried by a helium flow to the mass spectrometer. $\delta^{13}C$ values were reported relative to the V-PBD (Vienna Pee Dee Belemnite) standard and had an analytical uncertainty of 0.1 ‰. Further explanations of the analytical methods used for $\delta^{13}C$ in this study are available in Varsányi et al., (2011).

The remaining precipitate of the sample was used for radiocarbon analysis. The samples were treated with phosphoric acid while in a closed vacuum in order to release carbon as CO_2. Water was injected into the pre-vacuumed digestion reactor vessel through a septum-sealed cap by means of a sterile plastic syringe attached to a 0.45 um pore size membrane filter to filter out the particles from the samples during injection. Samples were heated for one hour at 80°C to facilitate CO_2 release. The released CO_2 gas was then transferred into a cleaning vacuum line, where all other gases was removed according to Molnár et al., (2013). In the vacuum line, the water was trapped in a dry ice trap, the CO_2 was trapped in a liquid nitrogen trap and all other gases were pumped away. The obtained pure CO_2 gas was then converted to graphite by sealed tube graphitization method (Rinyu, Molnár, Major, *et al.*, 2013). The ^{14}C measurements from the graphite targets were performed with a MICADAS accelerator mass spectrometer in the ICER laboratory. Fossil marble, as blank standard material (IAEA-C1, 0.0 pMC) and known age travertine reference material (IAEA-C2, 41.14 pMC) were also treated as control samples for the CO_2 extraction step, to determine if any modern/fossil carbon contamination was introduced during the extraction or graphitisation procedure. The overall measurement uncertainty for modern samples was < 3.0 ‰, including normalization, background subtraction, and counting statistics.

3.4. Results

Tritium, $\delta^{13}C$ and radiocarbon data are presented in Table 3. 1, using the aquifer host rock designations given in (van Gend *et al.*, 2020), along with HCO_3^- data obtained from the same source. HCO_3^- concentrations of groundwater in the Buffels River catchment generally range between 19.1 mg/L and 280 mg/L and concentrations increase with distance from the coast (Figure 3. 2).

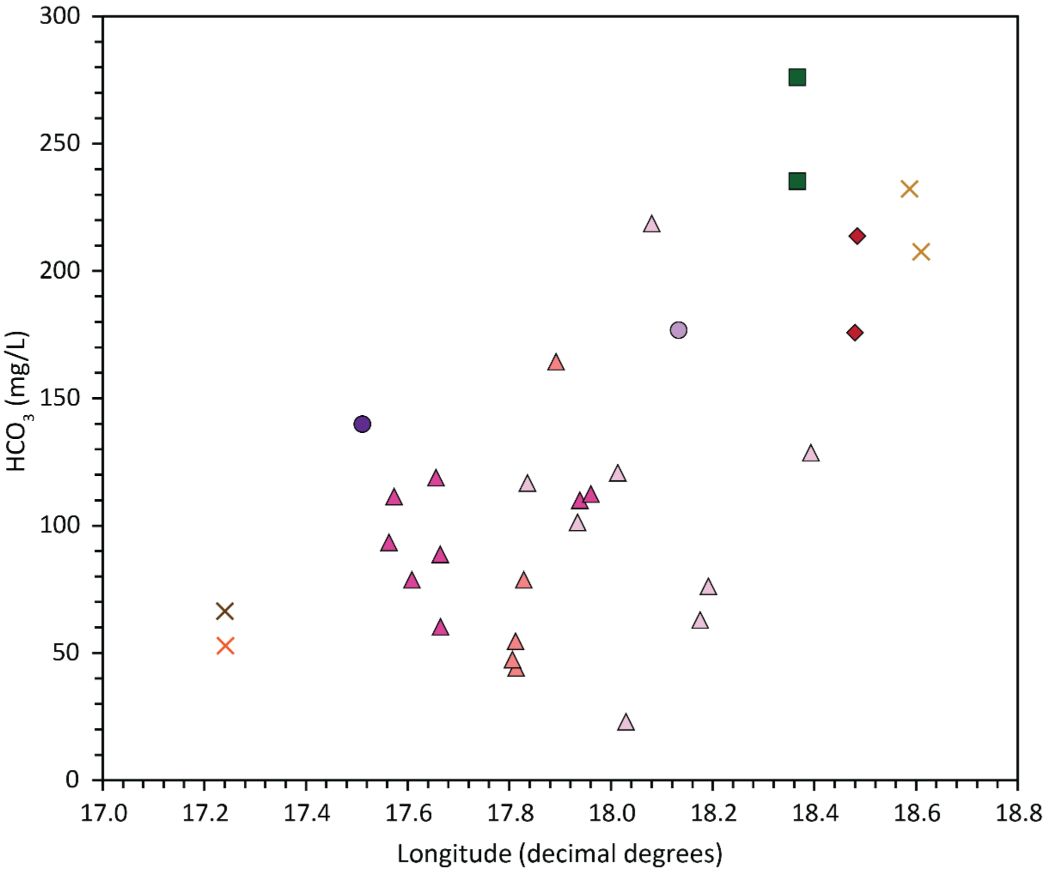

Figure 3. 2: Change in HCO_3 concentration with increasing longitude and therefore the change in $\delta^{18}O$ relative to the coast at a longitude of between 17.0 and 17.2 decimal degrees. See Figure 3. 1 for sample legend.

3.4.1. Tritium

Tritium activities in groundwater from the Buffels River catchment range between 0.08 TU and 1.58 TU (Table 3. 1). Groundwater with the lowest tritium activities was hosted by the Concordia Granites (n=5). The two samples with the lowest tritium activity of 0.08 and 0.09 TU were both collected from the plateau just east of the Buffels River Valley, while two samples collected within the valley, also hosted in the Concordia Granites, had higher tritium activities of 0.26 and 0.64 TU. Groundwater with the highest tritium activity of 1.58 TU was hosted by the Mesklip Granitic Gneiss (n=6). However, tritium activities of the remaining five groundwater samples hosted by the Mesklip Granitic Gneisses were all below 1 TU (Figure 3. 3). Although the lowest and highest tritium activities were found in groundwater hosted by the Concordia Granites and the Mesklip Granitic Gneisses respectively, groundwater tritium activities from both these host rocks were clearly variable. Groundwater hosted in the Modderfontein Granitic Gneisses of the Little Namaqualand Suite, record tritium activities between 0.21 TU and 0.63 TU, a much narrower range compared to that of the Mesklip Granitic Gneisses, which are also part of the Little Namaqualand Suite.

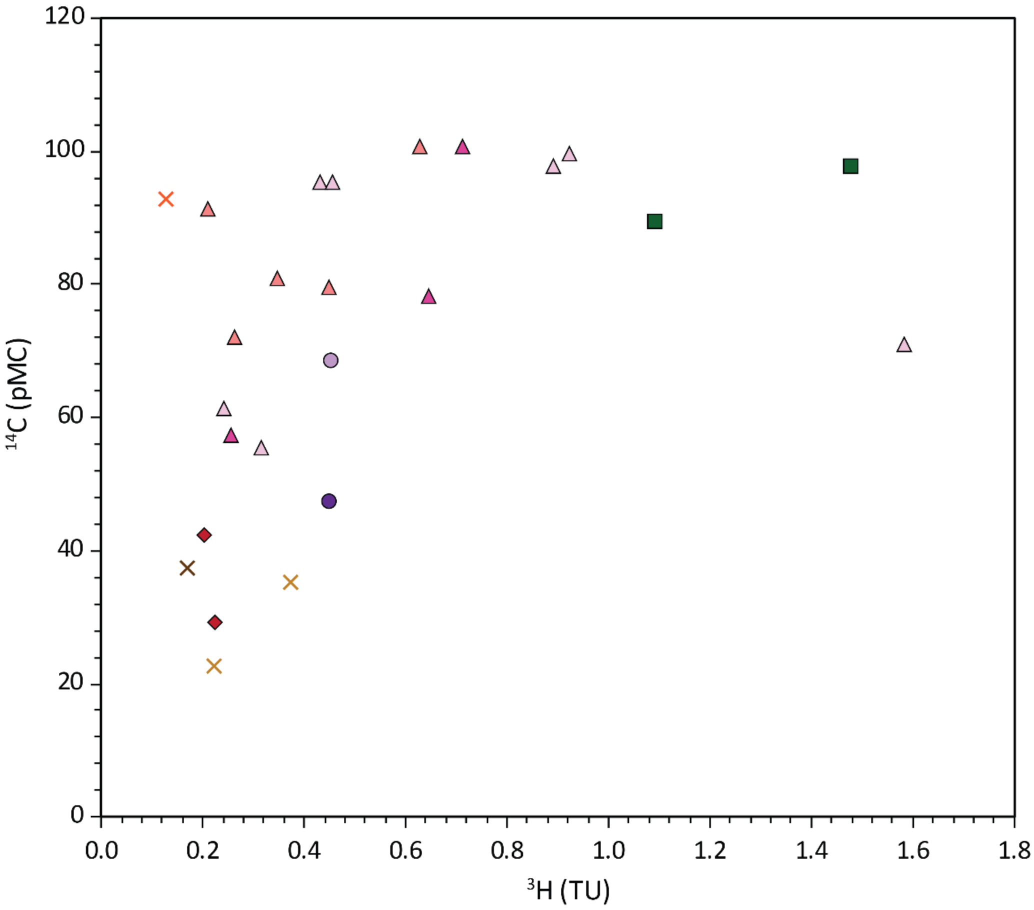

Figure 3. 3: ^{14}C activity compared to the tritium activity for groundwater collected in the Buffels River catchment represented according to the host rocks from which the samples were collected. Refer to Figure 3. 1 for the explanation of the symbology used.

Groundwater hosted in the alluvial sediments generally had low tritium activities irrespective of the borehole depth, with groundwater from the Platbakkies alluvial sediments having slightly higher tritium values than that collected from the Kleinsee sediments (Figure 3. 3). Sample KZ01 (shallow Kleinsee alluvial sediments), collected from a well of 3 m deep in the middle of the Buffels River bed close to the town of Kleinsee, had a tritium activity of 0.13 TU which is comparable to the tritium activity of sample KZ02 (deep Kleinsee alluvial sediments) of 0.17 TU that was collected in close proximity but from a borehole with a depth to groundwater of approximately 75 m. Groundwater hosted in the Lekkerdrink gneisses also indicated low tritium activities of 0.20 TU and 0.22 TU, while the two samples collected from the Gladkop Suite had higher tritium activities of 0.45 and 0.46 TU. Although only two samples were collected from the Kamiesberg Group, these samples both had high tritium activities (1.48 and 1.10 TU) compared to the rest of the host rocks in the catchment of which only one sample from the Mesklip granitic gneisses had tritium activity of more than 1 TU.

Table 3. 1: Tritium activity, radiocarbon activity and $\delta^{13}C$ values in groundwater. HCO_3 data was obtained from van Gend et al., (2020).

Suite/Group	**Pluton/Formation**	**Sample ID**	**BH depth (m)**	**^3H (TU)**	**^3H Error**	**HCO_3 (mg/l)**	**^{14}C (pMC)**	**^{14}C unc. (1s)**	**$\delta^{13}C$ sample/VPDB**
Little Namaqualand Suite	Shallow Kleinsee Alluvial Sediments	KZ01	3	0.13	0.06	52.80	92.7	0.29	-5.76
	Deep Kleinsee Alluvial Sediments	KZ02	75	0.17	0.06	66.40	37.4	0.21	-11.80
	Platbakkies Alluvial Sediments	KK09	23	0.22	0.08	207.60	22.6	0.10	-9.12
		KK10	45	0.37	0.07	232.20	35.3	0.12	-8.65
	Concordia granite	BR09	-	0.08	0.08	88.70	-	-	-
		BR05	65	0.26	0.05	93.40	57.4	0.29	-11.84
		BR10	30	-	-	60.30	100.0	0.41	-10.40
		BR17	-	-	-	118.90	40.3	0.25	-16.96
		BR19	-	0.09	0.04	78.70	-	-	-
		BR23	-	-	-	164.25	92.94	0.32	-11.35
		BR07	80	0.64	0.15	111.40	78.3	0.30	-11.76
		CD02	-	0.71	0.04	110.00	100.8	0.36	-
		CD03	-	-	-	112.40	77.5	0.34	-10.75
	Modderfontein granite/gneiss	NB01	75	0.26	0.03	44.10	72.2	0.31	-12.31
		NB02	-	0.63	0.04	47.40	100.7	0.38	-11.96
		NB03	-	0.21	0.04	54.60	91.3	0.33	-
		NB04	40	0.35	0.05	78.70	80.9	0.32	-
		SP02	-	0.45	-	164.40	79.6	0.25	-13.66

Suite/Group	**Pluton/Formation**	**Sample ID**	**BH depth (m)**	**^{3}H (TU)**	**^{3}H Error**	**HCO3 (mg/l)**	**^{14}C (pMC)**	**^{14}C unc. (1s)**	**δ ^{13}C sample/VPDB**
Little Namaqualand Suite	Mesklip granite	KK02	30	0.92	0.09	101.30	99.7	0.34	-13.03
		KK05	-	0.43	0.06	62.90	95.5	0.42	-4.95
		KK07	60	0.89	0.09	218.60	97.8	0.21	-7.44
		KK01	80	1.58	0.11	23.00	71.0	0.28	-13.84
		KK03	50	0.32	0.14	120.70	55.6	0.23	-16.16
		KK04	100	-	-	76.10	95.3	0.35	-
		KK12	86	-	-	128.60	63.8	0.30	-13.02
		SP01	-	0.24	0.05	116.80	61.4	0.23	-
	Lekkerdrink gneiss	KK08	70	0.22	0.07	175.80	29.3	0.12	-12.01
		KK11	150	0.20	0.10	213.70	42.3	0.13	-11.20
Supracrustal Rocks	Bushmanland Group	KG05	80	-	-	26.65	66.5	0.38	-10.58
		KG08	-	-	-	35.00	82.9	0.43	-11.85
	Kamiesberg Group	KK13	27	1.48	0.11	276.10	97.4	0.39	-11.56
		KK14	35	1.10	0.08	235.30	89.1	0.19	-11.67
Gladkop Suite	Noemnoemnaasberg granite	KK06	50	0.46	0.09	176.80	68.4	0.18	-12.39
	Steinkopf gneiss	SK01	100	0.45	0.16	139.90	47.2	0.22	-

3.4.2. δ^{13}C ratios

Groundwater δ^{13}C values varied between -17.0 ‰ and -4.95 ‰. Within this range, two samples had low δ^{13}C values of -17.0 and -16.2 ‰, 18 samples had δ^{13}C values between -13.8 ‰ and -10.4 ‰ and the remaining five samples had δ^{13}C values higher than -10.0 ‰. The δ^{13}C values were not necessarily consistent with the geological host rocks. Groundwater hosted by the Mesklip Granitic Gneisses had the most variable δ^{13}C values, ranging between -16.2 ‰ and -4.95 ‰ (n = 6) (Figure 3. 4). δ^{13}C values for groundwater collected from the Concordia Granite host rocks generally showed a narrower range in values between -10.4 ‰ and -11.9 ‰ with the exception of the one sample with the most negative δ^{13}C value of -17.0 ‰. Groundwater collected from the Modderfontein granitic gneisses also had little variation in δ^{13}C values and ranged between -13.7 ‰ and -12.0 ‰ (n = 3) (Figure 3. 4). The two samples collected from the Platbakkies alluvial sediments had δ^{13}C values of -9.12 ‰ and -8.65 ‰. The sample collected from the deep Kleinsee sediments had a δ^{13}C values -11.8 ‰, while the sample collected from the shallow Kleinsee sediments had a significantly higher δ^{13}C value of -5.76 ‰. Groundwater from the Lekkerdrink gneisses, Bushmanland Group and Kamiesberg Group, and Gladkop Suite were between -12.4 and -10.6 ‰ (n = 7) (Figure 3. 4).

3.4.3. Radiocarbon

Radiocarbon in groundwater in the Buffels River catchment were again variable ranging between 22.6 and 100.8 pMC (Table 3. 1). The lowest groundwater radiocarbon activity, 22.6 pMC, was from the Platbakkies alluvial sediments towards the east of the catchment. Similarly, the second sample collected from the same host and the sample collected from the deep Kleinsee Alluvial Sediments towards the west, also had low radiocarbon activities of 35.3 and 37.4 pMC, respectively. Groundwater hosted by the Lekkerdrink gneisses also indicated low radiocarbon activities of 29.3 pMC and 42.3 pMC (Figure 3. 4). Groundwater from the granitic gneisses of the Little Namaqualand Suite had higher radiocarbon activities ranging between 55.6 and 100.7 pMC (n= 13). The Concordia granites host groundwater with a slightly wider range of radiocarbon activities between 40.3 and 100.8 pMC (n = 7). The Gladkop Suite and the supracrustal rocks (Bushmanland and Kamiesberg Groups), hadradiocarbon activities of 47.2 and 68.4 pMC (n = 2) and 66.5 and 97.4 pMC (n =2) , respectively. Comparing the radiocarbon data with that of the tritium data, most samples showed higher tritium activities than expected for the radiocarbon activity (Figure 3. 3).

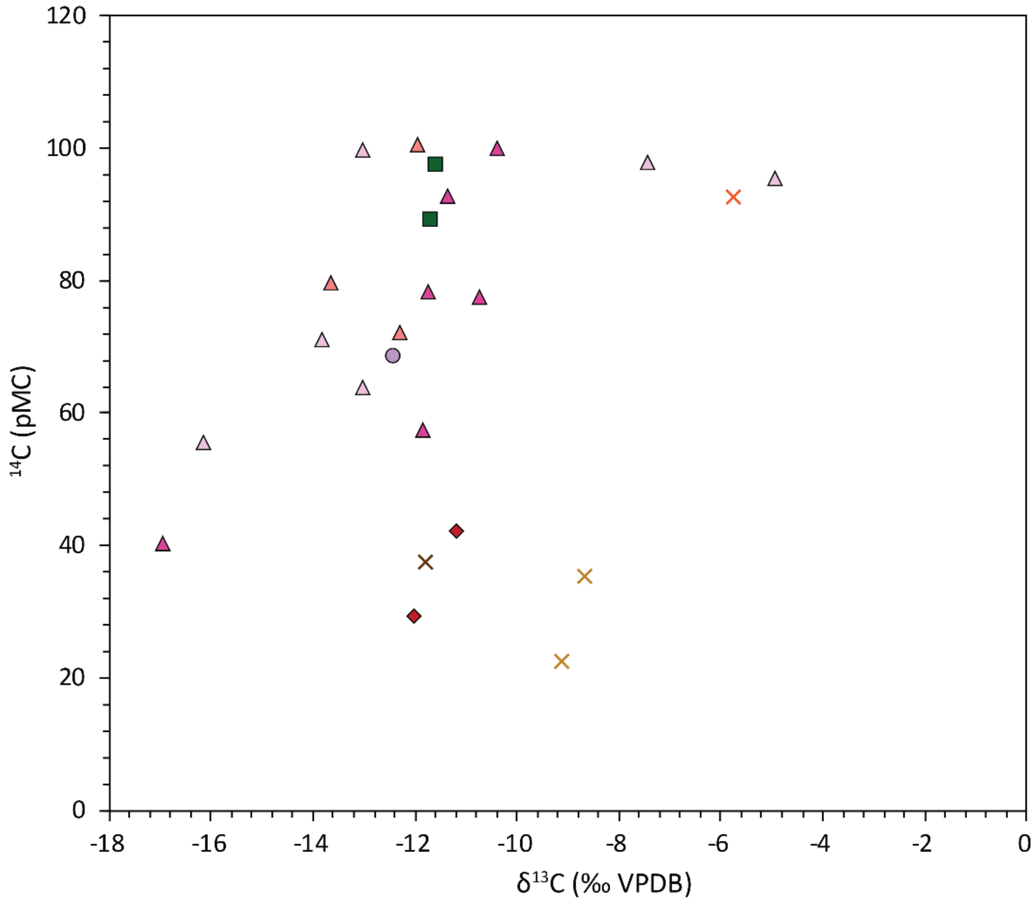

Figure 3. 4: ^{14}C vs δ^{13}C values for groundwater collected in the Buffels River catchment represented according to the host rocks from which the samples were collected. Refer to Figure 3. 1 for the explanation of the symbology used.

3.5. Discussion

The variability of the radiocarbon activity and the presence of tritium in groundwater together with the spatial distribution of saline groundwater (van Gend *et al.*, 2020) suggests that recharge pathways are not uniform throughout the catchment. Factors such as geology, the thickness of the soil horizons and the presence of heuweltjies, may and are likely to, influence these flow paths. Careful consideration of the conceptual recharge model or models for the region needs to be undertaken as this will influence how the groundwater residence time is calculated. In particular, the model should identify mechanisms that might change or dilute the radiocarbon signature in these aquifer systems and evaluate the likelihood of this occurring. Based on the conceptual model, the groundwater residence time was calculated using radioactive decay of the precursor ^{14}C isotope and with potential dilution of the radiocarbon addressed via a Pearson's mixing model approach. These results are compared to that of a lumped parameter model that accounts for the presence of tritium and hence components of modern recharge in an otherwise older groundwater system. Finally, the sustainability of groundwater in the Buffels River catchment in light the residence-time distribution is considered and the impact of future climate change on the availability of water resources and hence agricultural development in the area are discussed.

3.5.1. Current understanding of recharge in the Buffels River catchment

The known main recharge zone in the Buffels River catchment, the Kamies Mountains, is dominated by impermeable granitic gneisses in the form of Bornhardts where recharge pathways vary depending on the angle of the slopes and the conditions of the granite (i.e. degree of weathering). Extensive orthogonal fracture systems exist throughout the Bornhardts (Twidale, 2007), allowing for groundwater recharge to occur directly into the crystalline basement. However, the dome shaped geometry of the Bornhardts also causes runoff and ponding in the narrow valleys separating these granitic domes. In these valleys, thin vegetated soil horizons exist, impacting percolation through the unsaturated zone (Pietersen *et al.*, 2009). Here, the fracture frequency remains high and the weathered regolith, consisting of a combination of blocks of weathered and fresh granites derived from in situ weathering, extends deeper allowing for more effective recharge to occur (Titus *et al.*, 2009). In areas where ponding occurs and the fracture frequency in the underlying crystalline basement is low, isolated shallow alluvial aquifers may occur where the soils become saturated. From here, the groundwater can also move into the deeper basement system. However, groundwater recharge in the Buffels River catchment is not the same in all areas of the catchment. The two main alluvial aquifers in the catchment are both situated within the floodplain of the Buffels River and are recharged by infiltration during occasional flood events that are not deemed a sustainable water resource as significant recharge from floodwater is only received once every 5-10 years on average (Benito, Botero, *et al.*, 2011). The alluvial aquifers are also recharged through seepage, lateral flow and transmission along faults from the crystalline basement and this recharge may occur on a more regular basis during precipitation events that do not generate flooding (Benito et al., 2010; Watson et al., submitted).

3.5.2. Residence time of groundwater

Given this understanding of recharge in the Buffels River catchment, groundwater ages have previously been calculated by Adams et al. (2004) using conventional radiocarbon equations and modifications of the equation to account for some environmental factors which may have an effect on the age. These calculations are discussed in the below and validated in light of the new data collected during this study.

3.5.2.1. Radiocarbon age calculations

The conventional calculation for radiocarbon age, *t*, is:

$$t = \frac{5730}{\ln 2}\ln\left(\frac{A_0}{A}\right) \qquad \text{Equation 1}$$

where 5730 is the half-life of ^{14}C in years, A_0 is the initial ^{14}C activity, and *A* is the measured ^{14}C activity. This conventional radiocarbon age equation assumes that the activity of the ^{14}C isotope decreases as a function of radioactive decay only.

In natural systems, a number of processes may act to dilute the activity of ^{14}C which will give an artificially older age if calculated assuming only radioactive decay. To evaluate the dilution of the ^{14}C signal a number of correction processes have been proposed. One of the most common is that of Pearson (Ingerson & Pearson, 1964) although there are other similar approaches. In the Pearson model, $\delta^{13}C$ is used to correct for the dilution by assuming that the dilution affect will be the same for ^{14}C as it is for ^{13}C. Thus, the $\delta^{13}C$ for DIC in the groundwater can be compared to the $\delta^{13}C$ in the soil to evaluate dilution by using a dilution factor q defined as:

$$q = \frac{(\delta^{13}C_{DIC} - \delta^{13}C_{carbonate})}{(\delta^{13}C_{soil} - \delta^{13}C_{carbonate})} \qquad \text{Equation 2}$$

where $\delta^{13}C_{DIC}$ is from dissolved inorganic carbon in the groundwater, $\delta^{13}C_{carbonate}$ is the $\delta^{13}C$ value of carbonate rock or solid carbonate in the system, while $\delta^{13}C_{soil}$ is the $\delta^{13}C$ value of the soil which is governed by soil gas CO_2. This value is set by the biological activity such as the root respiration of C3 or C4 vegetation, microbial reactions or carbonates present in the subsurface or along the flow paths, or a combination of these processes. As water interacts with the soils and hence soil gas, the $\delta^{13}C_{soil}$ determines the $\delta^{13}C$ of the groundwater at that point and the primary $\delta^{13}C$ value of the groundwater is set at that point. The q value is incorporated into equation [1] as follows:

$$t = \frac{5730}{\ln 2} \ln \left(\frac{\mathrm{q} * {}^{14}\mathrm{C}_i}{{}^{14}\mathrm{C}_m} \right) \qquad \text{Equation 3}$$

where ${}^{14}C_i$ and ${}^{14}C_m$ are the initial and measured ${}^{14}C$ activity in the groundwater, respectively.

Residence times for groundwater in the catchment are thought to range between modern and ~32 850 years (Adams *et al.*, 2004). These ages were calculated using a uniform dilution factor of 0.85 for the samples that were collected from the basement aquifer in accordance with Hendry, (1988), who assigned this dilution factor to all hard rock aquifers. The ages for samples from alluvial aquifers were calculated without a dilution factor. For this study, when radiocarbon ages were calculated using Equation 1, the obtained residence times ranged between 23 years and 12 294 years, but also included two negative values implying ages into the future. If the groundwater residence times are recalculated using a uniform dilution factor of 0.85 consistent with the Adams et al. (2004) study, the ages range between 209 years and 10 951 years, but now includes 9 negative values. In both cases, the calculation of significantly younger ages, as well as the derivation of negative values indicates that the validity of assuming a uniform dilution factor is questionable. Interrogation of $\delta^{13}C_{DIC}$ values is necessary to resolve this issue but were not considered in the Adams et al. (2004) study.

The $\delta^{13}C_{DIC}$ of the groundwater in the Buffels River catchment is highly variable. This can either be a result of the variability in $\delta^{13}C_{soil}$ (hence variability in C3 or C4 plant species) or the $\delta^{13}C_{DIC}$ values are affected by dilution along the flowpath. However, both of these factors has an affect on the dilution factor and hence the age calculation of the groundwater. The $\delta^{13}C_{soil}$ for the Buffels River catchment is not known, but in general $\delta^{13}C_{soil}$ it is largely controlled by the dominant vegetation type of the area which in the case of the Buffels River catchment is mainly C3 with minor C4 species. The $\delta^{13}C_{soil}$ values of -24.0 ‰ and -10.0 ‰ in various ratios were used to represent the effect of C3 and C4 species, respectively (Appelo & Postma, 2005). The second component of Equation 2 is the $\delta^{13}C_{carbonate}$ that is dissolved and incorporated along the flow path. Typically, $\delta^{13}C_{carbonate}$ would result in strong dilution because most carbonate sequences are sufficiently old that they contain no ${}^{14}C$. The geology of the Buffels River catchment is silicate dominated and the current understanding is that there is no carbonate material along the flow path. However, given the variability in the $\delta^{13}C_{DIC}$ of the groundwaterand in the catchment and the fact that the $\delta^{13}C_{soil}$ is not known for this area, the value cannot be excluded from the calculation. Carbonates generally have $\delta^{13}C_{carbonate}$ values of between -2.0 and 2.0 ‰ (Oehlert & Swart, 2014; Plummer & Sprinkle, 2001) and a value of 0 ‰ was assumed for all samples.

Keeping in mind that a $\delta^{13}C_{carbonate}$ of 0 ‰ has been assumed and only changes in the $\delta^{13}C_{soil}$ are taken into consideration, 3 different q values can be calculated based on C3 specie dominated environment, a C4 specie dominated environment or an environment where C3 and C4 specie occur together in a ratio of 60% C3 and 40% C4 species which is likely to be the case in the Buffels River catchment (van Rooyen, 2020) (Table 3. 2). These dilution factors can then be used to calculate ages using equation 3. However, the dilution factors are highly variable and, in some cases, the calculated dilution factors are larger than 1.00. In addition to this, the described approach yielded many and almost exclusively negative ages suggesting that the dilution approach applied is not appropriate, as seen in Table 3. 2. Given that the current recharge model and the calculations associated with this model does not provide sensible radiocarbon ages, a new recharge model needs to be conceptualised.

Table 3. 2: Calculated groundwater ages using the conventional radiocarbon equation with various dilution factors. All ages given in years. The mixed values have been calculated based on 60% C3 vegetation and 40% C4 vegetation.

Sample ID	**No correction**	**Only Soil δ^{13}C values**						**Adams et al (2004)**
	Age	**q-value C3**	**Age C3**	**q-value mixed**	**Age mixed**	**q-value C4**	**Age C4**	**Age q = 0.85**
KZ01	622	0.24	-11108	0.31	-8911	0.58	-3871	-721
KZ02	8131	0.49	2330	0.64	4526	1.18	9567	6788
KK09	12294	0.38	4365	0.50	6562	0.91	11602	10951
KK10	8616	0.36	251	0.47	2448	0.87	7488	7273
BR05	4594	0.49	-1181	0.64	1016	1.18	6057	3250
BR10	-2	0.43	-6851	0.56	-4654	1.04	387	-1345
BR17	7509	0.71	4709	0.92	6905	1.70	11946	6166
BR23	606	0.47	-5518	0.62	-3322	1.13	1719	-738
BR07	2026	0.49	-3807	0.64	-1610	1.18	3431	682
CD02	-64	-	-	-	-	-	-	-1408
CD03	2109	0.45	-4464	0.58	-2267	1.07	2773	766
NB01	2695	0.51	-2757	0.67	-561	1.23	4480	1352
NB02	-54	0.50	-5743	0.65	-3547	1.20	1494	-1398
NB03	756	-	-	-	-	-	-	-588
NB04	1756	-	-	-	-	-	-	413
SP02	1891	0.57	-2698	0.74	-501	1.37	4540	548
KK02	23	0.54	-4959	0.71	-2762	1.30	2278	-1321
KK05	381	0.21	-12605	0.27	-10409	0.49	-5368	-962
KK07	187	0.31	-9422	0.40	-7226	0.74	-2185	-1156
KK01	2829	0.58	-1653	0.75	544	1.38	5584	1485
KK03	4852	0.67	1650	0.88	3846	1.62	8887	3508
KK04	396	-	-	-	-	-	-	-947
KK12	3715	0.54	-1274	0.71	923	1.30	5964	2371
SP01	4035	-	-	-	-	-	-	2692
KK08	10150	0.50	4497	0.65	6694	1.20	11734	8806
KK11	7113	0.47	878	0.61	3074	1.12	8115	5770
KG05	3372	0.44	-3329	0.58	-1132	1.06	3908	2028
KG08	1553	0.49	-4210	0.64	-2014	1.19	3027	209
KK13	214	0.48	-5757	0.63	-3561	1.16	1480	-1129
KK14	951	0.49	-4945	0.63	-2749	1.17	2292	-393
KK06	3138	0.52	-2261	0.67	-64	1.24	4977	1795
SK01	6205	-	-	-	-	-	-	4861

3.5.3. Conceptualisation of new model

$\delta^{13}C_{DIC}$ values for the groundwater in the Buffels River catchment are heterogeneous and can be explained by two separate scenarios or a combination of them. The first would be primary variation in the $\delta^{13}C_{DIC}$ values set by the $\delta^{13}C_{soil}$ value which is mainly controlled by different vegetation types in different areas within the catchment. This means that the $\delta^{13}C_{soil}$ values would reflect either C3 or C4 vegetation $\delta^{13}C$ or a combination of C3 and C4 vegetation, depending on the dominant vegetation in the region. As the water flows through the unsaturated zone, the original $\delta^{13}C_{DIC}$ values of the groundwater reflect the primary $\delta^{13}C_{soil}$ value of the soils which are heterogenous because of different proportions of C3 and C4 plants. The second scenario would be that the $\delta^{13}C$ values were originally more homogeneous and that dilution has taken place because of interaction with carbonate material along the flow path. For this heterogeneity to have occurred, some of the groundwater must have experienced different degrees of equilibration at different times causing changes in $\delta^{13}C_{DIC}$ and hence ^{14}C values of the DIC in the groundwater. In order to assess whether the processes outlined in these two scenarios played a role in dilution of ^{14}C signal, the recharge model described above needs to be modified.

The previous recharge model for this area by Adams et al. (2004) did not account for the heterogeneity in the $\delta^{13}C_{DIC}$, heterogeneity in the landscape caused by biophysical features, such as heuweltjies, or the possibility of carbonates with different ^{14}C values hosted in soils. In order to understand the heterogeneity, three conceptual recharge pathways were considered (Figure 3. 5). (1) direct recharge into the basement aquifer through the interconnected fracture network. As precipitation hits the surface of the exposed granites, water infiltrates directly through the fracture network. In this case the $\delta^{13}C_{DIC}$ of the groundwater will remain unchanged; (2) recharge is derived from percolation through soils, into the saturated zone. Here isolated alluvial aquifers may form above the granitic gneisses where groundwater can infiltrate into the basement aquifer if fracture networks allow for it; (3) recharge into the saturated zone and into the basement aquifer via heuweltjies where the tunnels (bioturbation / “termite” tunnels) act as preferential flow paths. In the third case, recharge may be considered relatively rapid where groundwater flows through the heuweltjies and into the saturated zone or onto the crystalline basement, depending on the soil thickness and heuweltjie size. From here, groundwater can infiltrate the basement aquifer through faults and fractures. For each of these pathways, potential recharge will be affected by different processes along the flow path that will in turn affect the residence time calculations. For the latter two models, variation in the $\delta^{13}C_{DIC}$ values is expected depending on the environment that the groundwater passes through before entering the crystalline basement.

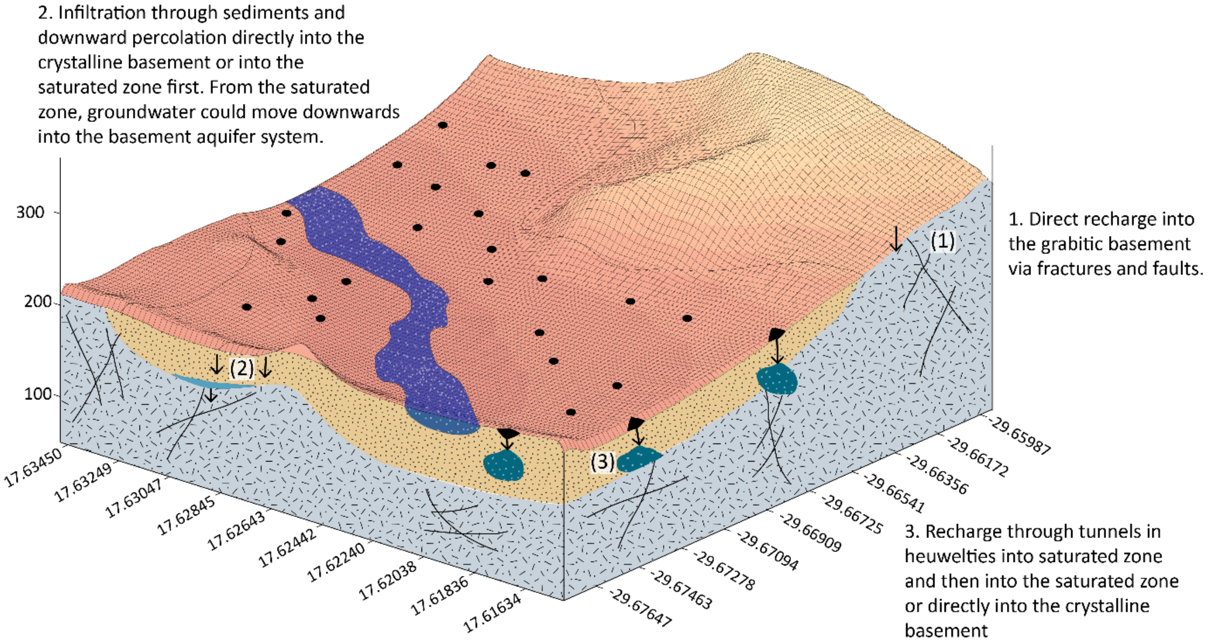

Figure 3. 5: Conceptual model showing the three proposed recharge pathways.

The heterogeneity of the $\delta^{13}C_{DIC}$ values in the Buffels River catchment can be summarised by three trends indicated on Figure 3. 6. (1) Change in the ^{14}C activity with no or very little change in the $\delta^{13}C_{DIC}$ values. This represents a closed system where decay occurs but there is no significant change in the $\delta^{13}C_{DIC}$ values. In this case it is likely that there were small variations in the initial $\delta^{13}C_{DIC}$ values when the groundwater entered the system but once it entered the crystalline basement, the ^{14}C activities changed only through radioactive decay and the $\delta^{13}C_{DIC}$ values remained unchanged as there aren't any carbonates in the aquifer matrix. In this case no dilution has occurred. (2) Change in $\delta^{13}C_{DIC}$ with no or very little change in the ^{14}C activity. This represents an open system where the ^{14}C activity remains in equilibrium with the atmosphere and therefore, no decay occurs but the $\delta^{13}C_{DIC}$ values are different for different samples. This would mean that the groundwater represented by these samples had different $\delta^{13}C_{DIC}$ values when it entered the aquifer. This is likely to be controlled by the $\delta^{13}C_{soil}$ values which are in turn controlled by vegetation type, soil type, carbonate formation within soils as well as biological activity. (3) Change in both ^{14}C and $\delta^{13}C$ values where ^{14}C decay occurs in combination with dilution in $\delta^{13}C_{DIC}$ values.

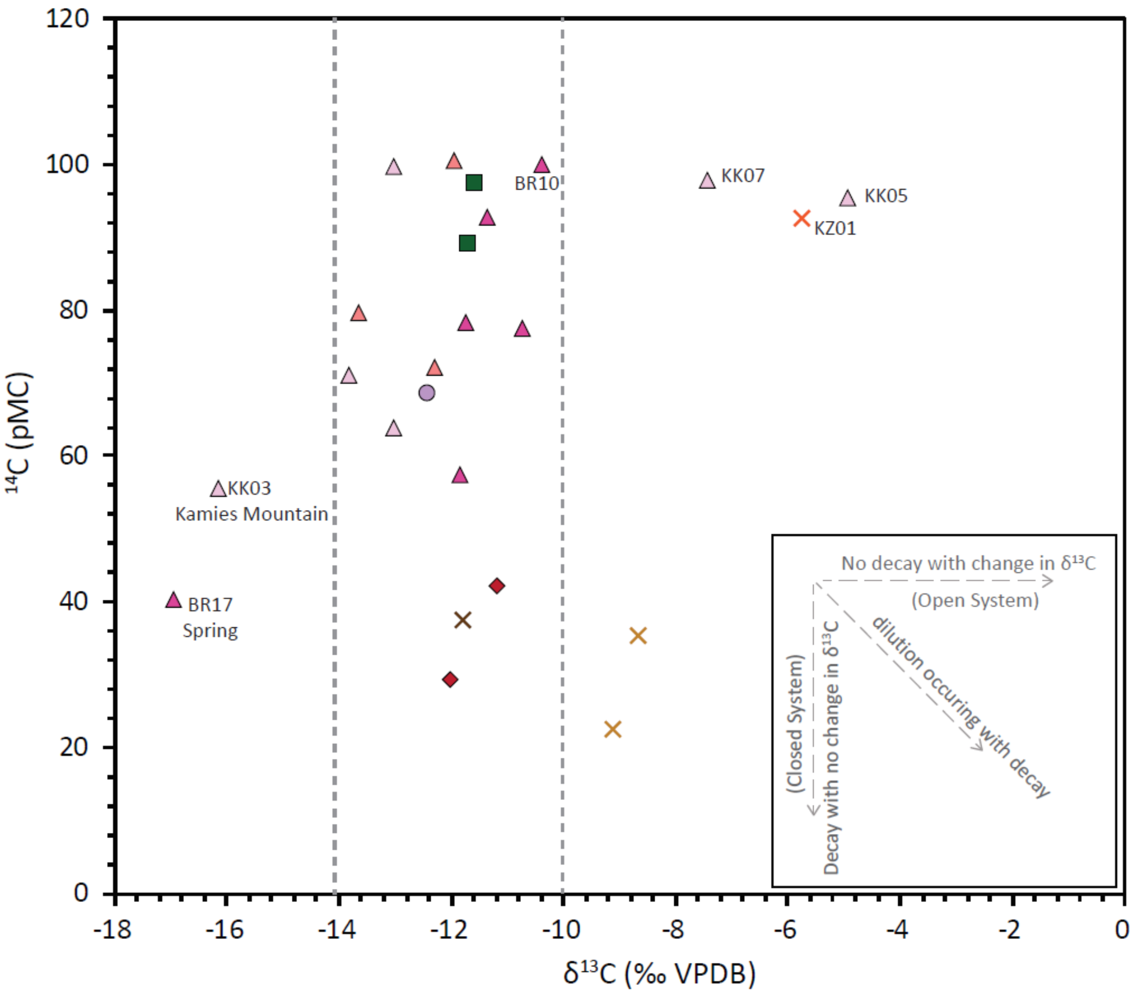

Figure 3. 6: ^{14}C vs δ^{13}C values for groundwater collected represented according to the host rocks from which the samples were collected. The dashed vertical lines group the set of samples that have small variation in the δ^{13}C values, that could have entered the system with these δ^{13}C values and have not been affected by dilution, but only decay. Refer to Figure 3. 1 for the explanation of the symbology used.

The processes that could have contributed to the difficulties in calculating groundwater ages in the Buffels River catchment using the conventional decay equations are variation in the primary ^{14}C value of the groundwater due to the interaction with soils with variable δ^{13}C$_{soil}$ or interaction with inorganic carbonates during recharge. Although the geology of the area and therefore the aquifer host rocks are dominated by silicates, inorganic carbonates in the form of calcite do occur in the soils of the Buffels River, specifically in the heuweltjie soils (Francis & Poch, 2019; Vermooten, 2019). These carbonates form within the heuweltjie as a result of a combination of decomposition of plant material that have been brought into the heuweltjie structure by the inhabiting termites and microbial processes (Francis & Poch, 2019).

Although the $\delta^{13}C_{DIC}$ values of groundwater in the Buffels River catchment may be affected by carbonates in the heuweltjies or the presence of C3 or C4 vegetation, groundwater percolating through the heuweltjies is still within the unsaturated zone. The system behaves as an open system where the radiocarbon activity is kept in equilibrium with atmospheric ^{14}C, but the $\delta^{13}C$ values may be affected by the carbonates or root respiration. Only once the groundwater has passed through the heuweltjies and reached the saturated zone, the system starts behaving as a closed system where the radiocarbon activity will start decreasing. Therefore, ^{14}C dilution (interaction with older carbonates) will also only have an effect when the groundwater reaches the saturated zone. This is seen in Figure 3. 6, samples KK02, BR10, KK07 and KK05, where a change in the $\delta^{13}C$ values are seen but the radiocarbon activity remains around 100 pMC. ^{14}C dilution will therefore only occur once the groundwater reached the saturated zone. Given that the aquifer matrix in the Buffels River catchment varies from place to place, groundwater chemistry and $\delta^{13}C$ values are affected by different processes in different areas and the groundwater residence times cannot be calculated in the same way for all the samples. To add to this, groundwater in the Buffels River catchment has detectable tritium activity with radiocarbon activities as low as 22.6 pMC implying mixing between younger and older waters via different pathways and in various proportions. For this reason, an alternative approach to calculating the groundwater residence time was used incorporating both tritium and radiocarbon as tracers to evaluate residence times and mixing relationships using a lumped parameter model (LPM) approach. This was done with the USGS TracerLPM program.

3.5.4. Modern recharge and theoretical mixing relationships

Given the presence of tritium in groundwater with low radiocarbon activities in the Buffels River valley, mixing of modern recharge with older groundwater seems likely. Conventional radiocarbon age calculations do not take this into account and therefore, lumped parameter models (LPM's) were used to calculate total mean ages of the groundwater. LPM's are transport based mathematical models that account for the effects of mixing within the aquifer system when determining age distributions or mean ages. It assumes that a sample consists of different parcels which have not necessarily followed the same flow paths and each parcel will therefore have specific tracer concentrations representing a specific groundwater age. LPM's calculate tracer concentrations at the outlet position or the sampling point from historical tracer data at the input location or recharge zone using exit-age distribution functions, decay functions and measured tracer data according to:

$$C_{out}(t) = \int_{-\infty}^{t} c_{in}(t')e^{-\lambda(t-t')} \cdot g(t-t') \cdot dt' \qquad \text{Equation 4}$$

Where $C_{out}(t)$ is the concentration of the tracer at the outlet, $C_{in}(t)$ is the concentration at the inlet at time t', the date when the water parcel entered the system while t is the sample date and λ the decay constant (Jurgens, Bohlke & Eberts, 2012).

The mean age of the sample (τ_S) is calculated using the exit-age distribution function that describes the tracer concentrations in the sample as seen in equation 4.

$$\tau_s = \sum_{i=1}^{\infty} t_i \, X_i(\Delta t) \qquad \text{Equation 5}$$

Where t_i is the age of the water parcel (t-t'), X_i is the fraction of the sample represented by the water parcel at a corresponding age increment while Δt is the age increment.

There is variation in possible recharge pathways in the Buffels River catchment and the new conceptual model takes most of these variations into account but as a broad overview. Recharge pathways have not been evaluated in detail and therefore, the mixing model used is rather theoretical than fully representative of the actual processes. In order to calculate the ages, a binary mixing model (BMM), incorporating both an exponential mixing model (EMM) and a piston flow model (PFM), was considered as in this theoretical approach, the combination of these models is the most representative of what could be occurring in the Buffels River catchment. The EMM assumes that uniform recharge is received over the entire area and that groundwater percolates through the unsaturated zone into the aquifer across the ground surface of the entire aquifer (Jurgens *et al.*, 2012). This is represented by the alluvial aquifers where groundwater moves through the unsaturated zone and into the saturated zone. In contrast, the PFM is more suited for fractured rock aquifer systems as it assumes that recharge occurs through specific conduits or fractures and groundwater exits through wells or springs (Jurgens *et al.*, 2012). Combining the two models allows incorporation of recharge into the fractured basement aquifer as well as the recharge that occurs within the valleys where water percolates through the soils. In the case where heuweltjies are present, the PFM model was still applied as the groundwater recharge will still enter through conduits or fractures, where these are represented by the tunnels and bioturbated soils on the heuweltjies. Historic tritium data from the IAEA's GNIP database for Cape Town and Windhoek was imported into the TracerLPM program and used to plot model tritium curves for the Buffels River catchment. Data from the Buffels River

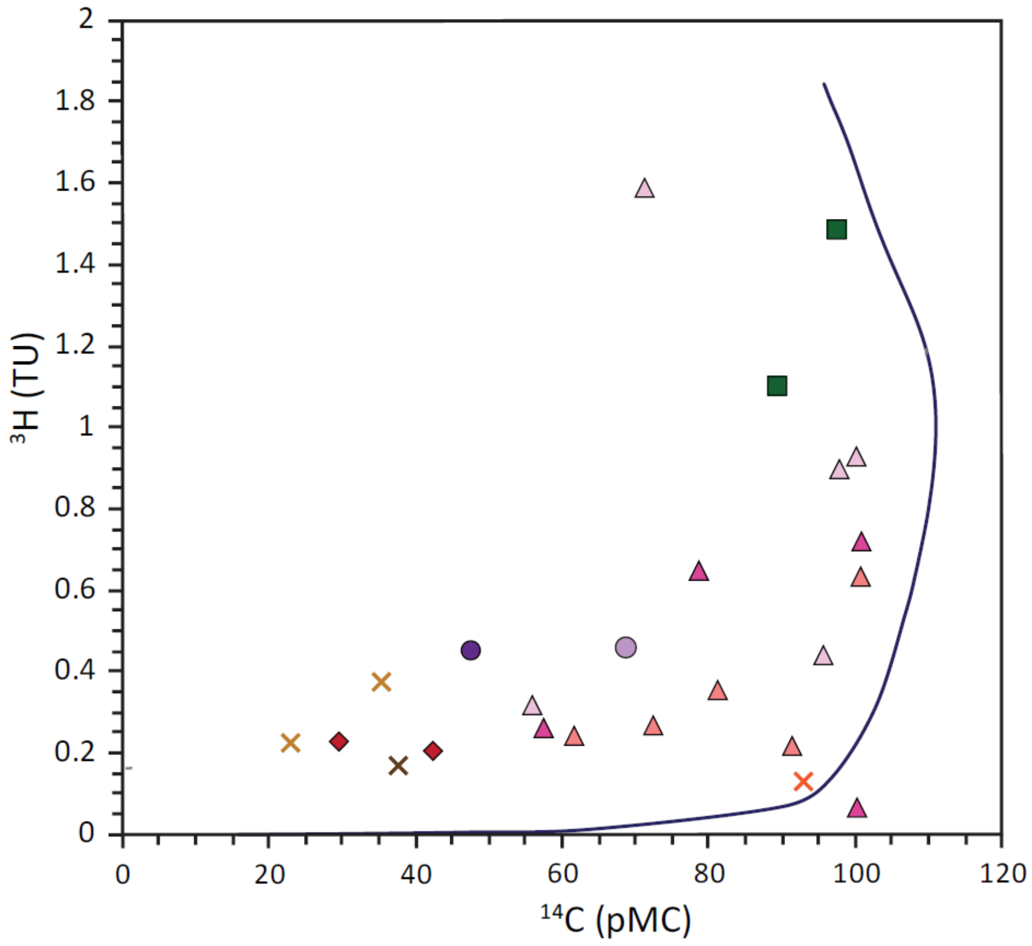

Figure 3. 7: Tritium activity vs radiocarbon activity for groundwater in the Buffels River catchment compared to the modelled LPM curve for tritium and radiocarbon activity in the Southern Hemisphere.

catchment is not available and of the available data, data from these two cities are the most representative of the catchment. For the radiocarbon curves, the preloaded TracerLPM data for the Southern Hemisphere was used as historic radiocarbon data for the west coast of South Africa is not available. Measured tritium and radiocarbon activities were plotted against the model generated using TracerLPM and the BMM-EMM-PFM binary mixing line was used to calculate the total mean age and the mixing fraction of the modern component (Figure 3. 7).

The calculated mean residence time of the groundwater in the Buffels River catchment varies significantly with very little geographic correlation. Tritium and radiocarbon values could not be obtained for all 37 samples, but of the 23 samples for which ages could be calculated using the theoretical LPM approach, only 4 samples have total mean ages that can be considered as modern (50 years and younger), while 12 samples have total mean ages that can be classified as young water with residence times between 50 and 12 000 years and 3 samples have total mean ages of older than

Table 3. 3: Groundwater age calculation data obtained by using LPM's

Pluton/Formation	**Sample ID**	**BMM-EMM-PFM**				
		Total mean age (years)	**Mean age of the modern component (years)**	**Modern fraction (modern component)**	**Mean age of the oldest component (years)**	**Relative error**
Shallow Kleinsee Alluvial Sediments	KZ01	552	6.2	8.0 %	600	0.79%
Deep Kleinsee Alluvial Sediments	KZ02	9409	2.2	9.5%	10400	0.84%
Platbakkies Alluvial Sediments	KK09	17794	2.0	12.4%	20300	0.01%
	KK10	12638	2.4	21.0%	16000	0.09%
Concordia granite	BR05	5346	2.4	14.5%	6250	0.20%
	BR07	2048	2.2	36.0%	3200	0.42%
	CD02	50	1.3	19.5%	62	0.53%
Modderfontein granite/gneiss	NB01	2778	1.8	14.6%	3250	0.00%
	NB02	49	6.5	23.5%	62	0.01%
	NB03	651	3.0	12.0%	740	0.05%
	NB04	1619	1.7	19.1%	2000	0.00%
	SP02	1908	4.2	26.7%	2600	0.00%
Mesklip granite	KK02	39	1.0	38.4%	62	1.17%
	KK05	301	3.3	25.0%	400	0.01%
	KK07	37	3.6	45.5%	65	0.05%
	KK01	-	-	-	-	-
	KK03	5647	1.1	17.0%	6800	0.00%
	SP01	4743	2.9	13.8%	5500	0.00%
Lekkerdrink gneiss	KK08	13567	2.0	12.5%	15500	0.00%
	KK11	8406	5.6	12.5%	9600	0.00%
Kamiesberg Group	KK13	21	1.2	80.00%	100	1.90%
	KK14	621	1.0	58.64%	1500	0.24%
Noemnoemnaasberg granite	KK06	3517	1.8	25.18%	4700	0.01%
Steinkopf gneiss	SK01	7954	1.0	24.25%	10500	0.99%

12 000 years which can be classified as fossil water (Table 3. 3). The total mean age of one sample could not be calculated as the tritium and radiocarbon activity of this sample are outside the modelled range. This could be due to a sampling or analytical error. Groundwater collected from the south east of the catchment generally has the lowest radiocarbon and tritium activity and the longest residence time, irrespective of host lithology with the three samples with total mean ages all collected from the south east of the catchment. However, groundwater collected from the Kamiesberg Group which were also collected from the east of the catchment, but slightly to the north of the previously mentioned samples, have higher radiocarbon and tritium activities with residence times of 21.0 and 621 years in which case the groundwater is classified as modern to young. This is also the case for groundwater in the known recharge zone of the catchment, as well as in the central and northern parts of the

catchment, where groundwater ages range between 38.6 and 5657 years. The two samples collected from far west of the catchment have total mean ages of 553 and 9409 years. This is interesting because both of these samples were collected from sediment host rocks but the younger of the two samples was collected from a large open well with a depth of 3 m in the centre of the dry Buffels River which suggests that the water in this alluvial setting is being recharged by a significant component of older groundwater via lateral flow from the deeper system which in this case is not a pure fractured system but a deeper alluvial system. The second and older sample from this area indicates that the Deep Kleinsee Alluvial sediments hosting older groundwater is present in this region (Table 3. 3).

3.5.5. Robustness of groundwater ages

Previous studies indicated that groundwater in the Buffels River catchment is up to 32 850 years old (Adams *et al.*, 2004). However, these ages were calculated using the conventional decay equation and a dilution factor of 0.85 for all samples, irrespective of host rock geology or variation in $\delta^{13}C_{soil}$ values. In this study, three conventional calculation methods were evaluated. 1) the conventional equation with no correction; 2) the conventional equation with a dilution factor based on the $\delta^{13}C_{soil}$ values of each sample; and 3) the conventional equation with a dilution factor of 0.85 for all samples as was done by Adams et al., (2004). In all cases, some negative age values were obtained, and the ages were generally much younger than what was previously thought. These conventional methods are therefore questionable and an LPM approach was used to obtain total mean groundwater ages. However, there are some flaws in using this approach for this specific study. 1) LPM's are usually used for relatively complex binary mixing models where the recharge pathways are well understood and constrained. In this case, it was used for a simplified conceptual recharge model and there is a possibility that the LPM used here is oversimplified; 2) The historical preloaded database in Tracer LPM for atmospheric radiocarbon for the Southern Hemisphere is small compared to that of the Northern Hemisphere and most of the data is from New Zealand. However, this database is one of the only available for the Southern Hemisphere which could cause some degree of error when used to model groundwater ages in semi-arid to arid southern Africa; 3) It is assumed that tritium activity in groundwater is only from modern recharge but atmospheric contamination is not taken into consideration. If atmospheric contamination has occurred in the sampling process or even along the flow path, the radiocarbon ages will appear much younger than what they actually are, irrespectively of the calculation method. This is therefore also applicable to the conventional methods used to calculate the ages in section 3.5.2.

Although there are some flaws in using LPM's to calculate the total mean age of groundwater in the Buffels River catchment, it does provide valid ages with small apparent error values. In addition to this, the spatial distribution of the percentage modern recharge of samples collected in the same region within the catchment are comparable irrespective of the calculated age, providing an indication that changes in the actual system are consistent with what is seen in the model. In contrast to this, the conventional age calculation methods rely on a dilution factor that could potentially be highly variable across the catchment. The ages calculated using no dilution factor as well as four different possible dilution factors all generate negative ages are regarded as not reliable. In order to get more accurate ages using the conventional approach, the factors that could contribute to radiocarbon dilution will have to be evaluated for each sample individually. This will have to include C3 and C4 plant distribution, soil and soil gas δ^{13}C. In addition to this, the presence of carbonates in the soil will have to be evaluated and the way it interacts with water as it percolates though the soils.

3.5.6. Groundwater salinisation and sustainability

Groundwater plays a significant role in the Buffels River catchment in terms of sustaining the domestic needs of the communities, the local economy, food security and the natural eco-system. Even though this region is classified as an arid environment and most species are adapted to survive in these conditions, climate change predictions suggest this may change. Globally, rainfall events are likely to become more erratic and intense and periods of extreme drought are expected to be more frequent and last for longer periods (Gizaw & Gan, 2017; Masih, Maskey, Mussá, *et al.*, 2014), which is also expected in the Buffels River catchment. Coastal fog will decrease(Davis *et al.*, 2016; Weldeab *et al.*, 2013) affecting the natural ecosystem which currently relies on fog and the dependence on groundwater to sustain the agricultural sector as well as the natural eco-system will increase. Most of the towns in the catchment are already wholly dependent on groundwater and in some cases, boreholes have dried up which has forced farmers and the local authorities to further tap into the groundwater system or reduce agricultural activity significantly. Given that only 4 of the 23 samples can be classified as modern in terms of the description given by Bierkens & Wada, 2019; Gleeson et al., 2016; Jasechko et al., 2017; Margat et al., 2006, together with the current climate predictions and the recent drought resulting in drying up of boreholes, there is a risk of groundwater depletion in the Buffels River catchment. This will specifically have an impact on the agricultural sector as there are very few, if any, flora or fauna species that are able to naturally survive in these climatic conditions that can be cultivated or kept on a large scale, without a reliable source of water, that will play a role in sustaining the economy or food security.

Apart from the risk of groundwater depletion in the region, further deterioration of the groundwater quality will be detrimental to the social and economic development of the region. However, salinisation of groundwater in the Buffels River catchment is a natural process controlled by various factors, including the saline heuweltjie soils. Although the exact mechanism of groundwater salinisation through heuweltjies have not yet been determined, heuweltjies are such pronounced features, not only in the Buffels River catchment, but along the west coast of southern Africa, that the effect that these saline features may have on the groundwater quality cannot be overlooked. With rainfall events likely to become more erratic but also more intense, salts sored in heuweltjies are likely to be washed into the groundwater system more regularly, speeding up the groundwater salinisation process. In addition to groundwater salinisation, saline heuweltjie affected soils limits agricultural and hence economic development. These soils cannot be used for agricultural purposes as very few crops will be able to tolerate the extreme soil salinity together with the semi-arid to arid climatic conditions and the lack of sufficient irrigation or the salinity of the groundwater used for irrigation.

3.6. Conclusion

The sustainability of groundwater both in terms of quantity and quality is a major issue in the Buffels River catchment. In order to better understand this issue, the age of the groundwater was determined to gauge recharge times as well as the possible period of salinisation. The absence of inorganic carbon in the geology and the uncertainty about the presence of inorganic carbon along the groundwater flow paths resulted in challenges in using the conventional radiocarbon age calculation methods. A new conceptual flow model was constructed to include three possible groundwater flow paths 1) direct recharge into the basement aquifer, 2) percolation through sediments, into the saturated zone and depending on the presence of a fracture network, into the granitic basement; 3) through heuweltjies and either directly into the granitic basement or into the saturated zone and then following the same process mentioned in pathway 2. Due to the presence of tritium in samples with lower radiocarbon activities and the uncertainties whether radiocarbon dilution could occur in the system, a simplified and theoretical LPM model was used to calculate total mean groundwater ages. Groundwater in the Buffels River catchment is generally older than 300 years (young groundwater between 50 and 12 000 years) with only 4 of the samples being modern, while groundwater in the east of the catchment is fossil groundwater of older than 12 000 years. Although modern recharge does occur, the percentage of the modern component in most cases are relatively small, indicating that the recharge occurring is not necessarily sustainable and water that is currently being abstracted is not modern water.

3.7. References

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CHAPTER 4.

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Mechanisms and timing of groundwater salinisation in Buffels River catchment.

J van Gend[1], M Francis[3], L. Palcsu[2], C.E. Clarke[3], J.A. Miller[1*]

1. *Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, South Africa*
2. *Isotope Climatology and Environmental Research Centre, Debrecen, Hungary.*
3. *Soil Science Department, Stellenbosch University, Private Bag, X1, Matieland, South Africa*

* Corresponding Author: E-mail address: jmiller@sun.ac.za.

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Abstract

There is a close relationship between saline groundwater and semi-arid to arid environments. However, in the case of the Buffels River catchment and large parts of the west coast of southern Africa, this relationship is not a result of evaporative concentration of salts followed by flushing of these salts into the groundwater. This study indicates that saline groundwater along the west coast of southern Africa is partly caused by heuweltjies where these large termite (*Microhodotermes viator*) mounds, comprise up to 25% of the landscape. Calcite present in heuweltjies were dated using radiocarbon age dating methods and it was found that heuweltjies are up to ~30 000 years old. The depths of calcite horizons, which can be related to mean annual precipitation, showed that three wetting fronts which specifically indicated that termite activity along the west coast facilitate groundwater flow. Groundwater chemistry and ages where compared to the carbonate ages in the heuweltjies and to past climatic events to determine whether there were specific periods during which the salts in heuweltjies could have been flushed into the groundwater system. Increases in anion concentrations were related to wetter periods in the past, while very little change in groundwater chemistry was seen during the past drier periods. The hypothesis that saline groundwater and heuweltjies are related was confirmed by comparing $\delta^{34}S\ SO_4^{2-}$and $\delta^{18}O\ SO_4^{2-}$ in heuweltjie soils to that of groundwater. In areas were the heuweltjie density increases, the $\delta^{34}S\ SO_4^{2-}$and $\delta^{18}O\ SO_4^{2-}$ signatures of groundwater and heuweltjie soils are comparable, a “granitic gneiss”-influence is seen in the fractured aquifer where the heuweltjie density is low.

4.1. Introduction

Climate change has been one of the main factors controlling human activity and populations for thousands of years (Dewar & Stewart, 2017; Rothacker, Dosseto, Francke, *et al.*, 2018). Sub-Saharan Africa is one of the regions that will suffer most from the impacts of climate change (Connolly-Boutin & Smit, 2016; Kotir, 2011). This is partly due to the region's dependence on natural resources and low ability to adapt (Thornton *et al.*, 2008). The lack of information about this region and the fact that technological change is the slowest in this region also contribute to the region's vulnerability to the effects of climate change (Kotir, 2011). In addition to this, it is expected that more than half of the global population increase expected by 2050, will occur in sub-Saharan Africa (WWAP - UNESCO World Water Assessment Programme, 2019), a region where water resources are already stressed. Currently, only 24% of sub-Saharan Africa receives water from safely managed water services and 58% of the global population drinking water directly from the surface water source, live in this region (WWAP - UNESCO World Water Assessment Programme, 2019).

In Namaqualand, a coastal desert region in south-west Africa, in the Northern Cape of South Africa, records of the effects of climate change on human populations since the Mid-Pleistocene have been preserved (Dewar & Stewart, 2017). These records can provide answers to many of the uncertainties of future climate change predictions. In the past, Namaqualand was colonised and abandoned regularly as a result of the shifts from periods of extreme drought to wetter and more habitable periods (Dewar & Stewart, 2017). Climate change predictions for Namaqualand include increasing temperature and changes to the rainfall amounts and patterns, specifically along the coastal region where rainfall is expected to decrease significantly (MacKellar, Hewitson & Tadross, 2007). As the dry areas become drier and the wet areas wetter (Davis *et al.*, 2016; MacKellar *et al.*, 2007), the stress on surface water resources in large parts of sub-Saharan Africa will increase and some water sources may even dry up, shifting the stress to groundwater resources as the main source of water (MacDonald, Bonsor, Calow, *et al.*, 2011).In modern times populations are not necessarily able to shift to more habitable climate zones as they did in the past, and climate change adaptation strategies are put in place to cope with climate change. However, with these strategies come the increased use in groundwater in a region already relying on groundwater as one of the only sources of potable water. In addition to this, the groundwater in this region is variably saline (van Gend *et al.*, 2020) and the possibility of further salinisation together with possible depletion of the water resources will be detrimental to this region. Groundwater salinisation in semi-arid to arid regions is typically ascribed to evaporative concentration of salts in soils after which the salts are flushed into the groundwater system during episodic precipitation events (Nogueira, Stigter, Zhou, *et al.*, 2019). However, in Namaqualand, the main sources of salts is dry deposition of marine aerosols which is being flushed into the aquifer system and water-rock interaction (van Gend *et al.*, 2020).

The aim of this paper is to determine the mechanisms and timing of salt input in the groundwater of the Buffels River catchment. Results from previous studies have shown that salts present in the groundwater are linked to dry deposition of marine aerosols and ion-exchange reactions between the aquifer host rock and the groundwater (van Gend *et al.*, 2020). This suggest leaching of marine-originated salts to reach groundwater, which is a paradox given the aridity of the region. The hypothesis is that the wetter and more humid periods are responsible for flushing salts from the regolith into the groundwater system, and that this effect is amplified by the presence of preferential flow paths associated with the hotspots of saline, termite-affected soils (heuweltjies) that are so striking in the catchment. By understanding the mechanism and timing of salinisation in this region, groundwater management and climate change strategies for Namaqualand can be adapted to include the possible causes and risks of salinisation.

4.2. Environmental context

The Buffels River catchment is situated in a semi-arid to arid Namaqualand region in the Northern Cape of South Africa. The catchment is approximately 9250 km^2 in size and stretches across three rainfall zones. The western section and towards the centre of the catchment rainfall generally occurs in winter, while the eastern section receives yearly and summer rainfall. The mean annual precipitation (MAP) varies across the catchment with hyper-arid conditions along the coast with a MAP of 50 mm/year, while the coastal plain receives around 110mm of rain per year (Benito, Thorndycraft, *et al.*, 2011). The Kamies Mountains in the south of the catchment has the highest MAP of more than 400 mm/year (Benito *et al.*, 2010). Heavy dewfall in winter and fog received in the summer plays a significant role in sustaining the environment, specifically in terms of vegetation (Davis *et al.*, 2016). Summer temperatures often exceed 35°C during the day while the average daily temperature in winter is 17°C. In winter, the temperature drops significantly at night and can reach sub-zero.

4.2.1. Heuweltjies

Heuweltjies, mound shaped biophysical features of up to 60 m in diameter (van Gend *et al.*, 2020), are common features along the west coast of southern Africa comprising up to 25% of the land fraction in western South Africa (Lovegrove & Siegfried, 1989). Although there is still some controversy around the mechanism of formation, many authors agree that heuweltjies are associated with termite activity (McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Moore & Picker, 1991b; Picker *et al.*, 2007; Potts *et al.*, 2009). More specifically, heuweltjies host the long-lived nests of the southern harvester termite, *Microhodotermes viator* (Figure 4. 1b)(Moore & Picker, 1991b), and in the Buffels River multiple nests are present in a single heuweltjie (Vermooten, 2019). As a result, heuweltjies soils are highly bioturbated and large tunnels of up to 3 cm in diameter exist throughout the heuweltjie (Figure 4. 1a and c), with the highest concentration of tunnels around the nests (Figure 4. 1). Heuweltjie soils are nutrient and salt rich and aerated (Francis & Poch, 2019; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Midgley & Musil, 1990), with the nutrient and salt density increasing towards the middle of the heuweltjie as well as with depth (van Gend *et al.*, 2020). Heuweltjies generally consist of more sodic and calcareous soils than their surroundings, typically enriched in silica and are often associated with silica-cemented dorbank (duric or petroduric (IUSS Working Group WRB, 2015)) lenses (Francis *et al.*, 2007). The common salts present in heuweltjies are halite, gypsum, and calcite, with calcite being the most abundant, often as full horizons within the heuweltjies (Francis & Poch, 2019; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; Vermooten, 2019). Heuweltjie soils are therefore often lighter in colour than the surrounding (interheuweltjie) soils making them easily identifiable on aerial imagery.

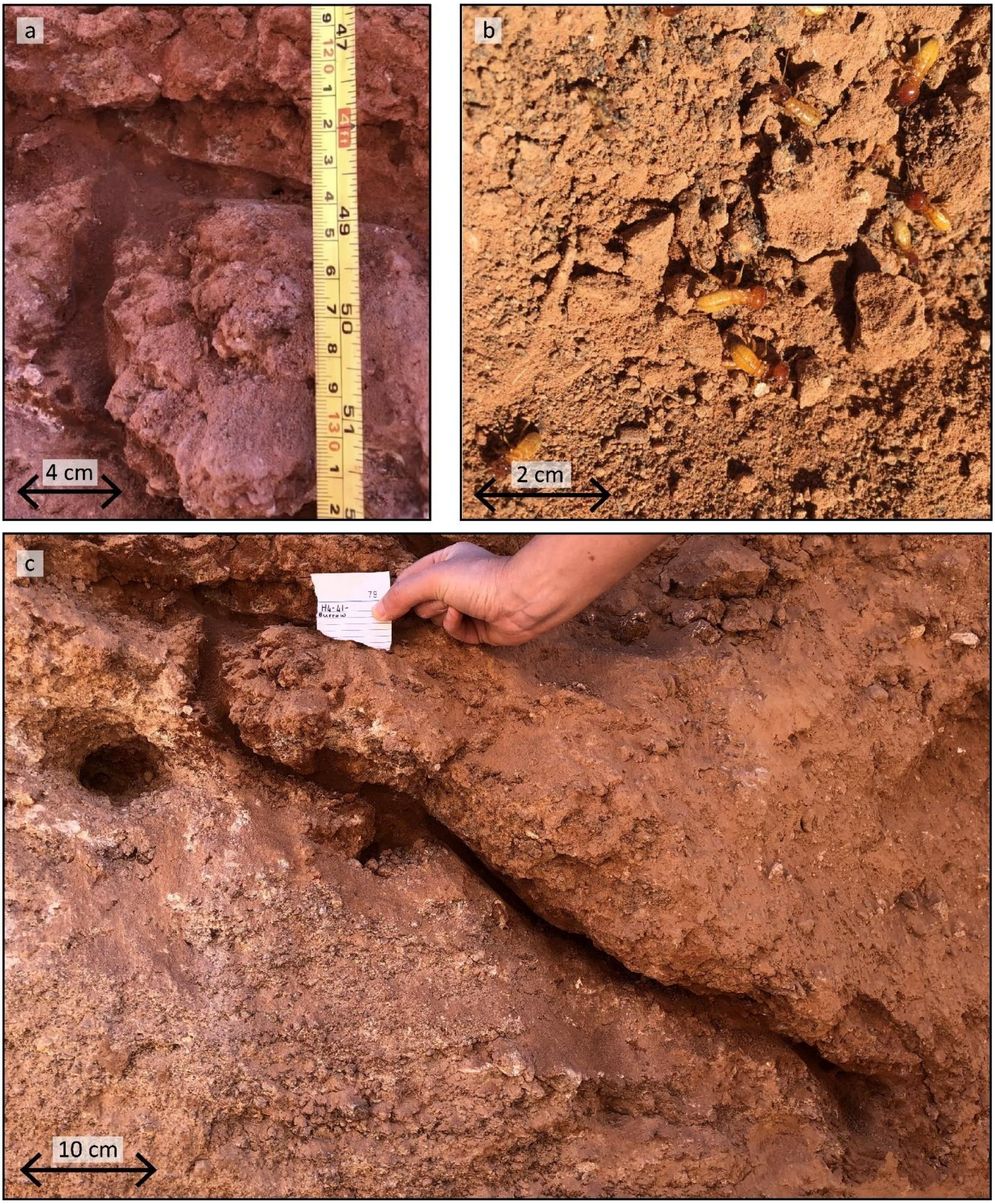

Figure 4. 1: Termite tunnels in heuweltjies. a) tunnels up to 4 cm. b) *Microhodotermes viator* on the heuweltjie surface, entering the heuweltjie through tunnels. c) large tunnel extending downwards in the heuweltjie.

4.2.2. Geology

The geology of the Buffels River catchment is dominated by granitic gneisses of the Bushmanland Sub-Province of the Namaqua Sector of the Namaqua-Natal Metamorphic Province. The lithostratigraphy is broadly comprised of deformed granitic gneisses and strongly remelted supracrustal rocks (Cornell, Thomas, Moen, *et al.*, 2006; Macey *et al.*, 2018; Thomas, Gibson, Moen, *et al.*, 2016). The Gladkop Suite, the oldest of the Bushmanland Subprovince mainly occurs in the north of the catchment with minor outcrops in the south (Robb *et al.*, 1999), while the Lekkerdrink gneisses occur mainly in the south (Macey *et al.*, 2011) (Figure 4. 2). The Little Namaqualand Suite, consisting of the Modderfontein and Mesklip granitic gneisses, crops out throughout the catchment, typically dominating the mountainous landscapes (Macey *et al.*, 2018). In the central part of the catchment, to the north and west of the town of Springbok, the Concordia granites are dominant with the granitic gneisses of the Spektakel Suite co-occurring towards the north and north-west of Springbok (Figure 4. 2). Meta-sedimentary and meta-volcanic supracrustal gneisses of the Bushmanland and Kamiesberg Group occur as lenticular belts between the granitic gneisses (Cornell *et al.*, 2009; Raith *et al.*, 2003). The granites and gneisses are unconformably overlain by the sedimentary rocks of the Nama and Vanrhynsdorp Groups in the Buffels River valley and towards the north (Blanco, Germs, Rajesh, *et al.*, 2011; Gresse, 1995). To the east and west of the catchment, sediments overly the basement geology. Red aeolian sediments dominate towards the east while the fluvial sediments overlain by marine sediments of the Buffels Marine Complex occur on the coastal plain towards the west (Francis *et al.*, 2007; Roberts *et al.*, 2014, 2009). These sediments are capped by coastal dune fields(Roberts *et al.*, 2014).

4.2.3. Groundwater in the Buffels River catchment

Two main aquifer systems exist in the Buffels River catchment namely shallow alluvial systems and deeper fractured systems where groundwater is hosted in the basement granitic gneisses. The shallow alluvial systems are mainly smaller isolated systems which formed in sand filled basins above the irregular surface of the basement geology (Benito, Botero, *et al.*, 2011). These systems are closely interlinked with the fractured system in areas where the basement rocks contain more faults and fractures (Titus *et al.*, 2009). Groundwater in the deeper basement aquifer systems are hosted in fractures and faults within the granitic gneisses. The basement aquifers cover larger areas, but the groundwater chemistry is highly variable across the catchment. The groundwater is generally highly saline (EC values up to 5556 µS/cm) with sodium and chloride being the dominant ions in all the groundwater samples, irrespectively of the aquifer host rock (van Gend *et al.*, 2020).

4.2.3.1. Groundwater flow paths and age model

The landscape of the Buffels River catchment does not allow for groundwater to enter the various alluvial and fractured aquifer systems in the same way. The Bushmanland Plateau towards the east of the catchment, comprises of gently undulating basement rocks covered by thick sedimentary layers. Here both fractured and alluvial aquifer systems exist (Benito *et al.*, 2010). Along the Namaqualand highlands or the escarpment, Bornhardts, extensively fractured granitic domes, dominate the landscape (Twidale, 2007). The thickness of the sediments in the valleys between these domes vary and groundwater is mostly hosted in fractured systems (Titus *et al.*, 2009). The western part of the catchment forms part of the coastal lowland where the basement rocks are overlain by much younger sediments (Francis, 2008). This is also the region where the heuweltjie density increases and both fractured and alluvial aquifers exist. Given these geomorphological differences across the catchment together with the heterogeneity of $\delta^{13}C_{DIC}$ values in the groundwater, the new groundwater model was conceptualised (Chapter 3, Section 3.5.3, page 87). Three pathways are highlighted, 1) direct recharge into the fractured basement system through the extensive fracture networks; 2) percolation of groundwater through soils and into the saturated zones above the basement rocks, from where it can enter the fractured system if the fracture networks allow it; 3) recharge through heuweltjies via preferential flow paths into the saturated zone above the basement geology from where it can enter the fractured zone through the fracture network.

Chapter 3 revealed that groundwater flow paths are not uniform and that $\delta^{13}C_{DIC}$ values of groundwater in the Buffels River catchment is not homogeneous and hence groundwater ages cannot be calculated using conventional methods. In addition to this, groundwater in the Buffels River with low radiocarbon activities, contain traces of tritium implying that mixing between younger and older waters via different pathways and in various proportions. Total mean groundwater ages were calculated using tritium and radiocarbon activities as tracers with a simplified lumped parameter model. The model is based on historical local tritium data and historical radiocarbon data for the Southern Hemisphere (Chapter 3, Section 3.4.5, page 90). Each of the samples were treated individually to assess the possible mixing relationships to calculate the total mean age of the sample. These total mean ages range between modern and ~18 000 years old with the groundwater towards the east being the oldest.

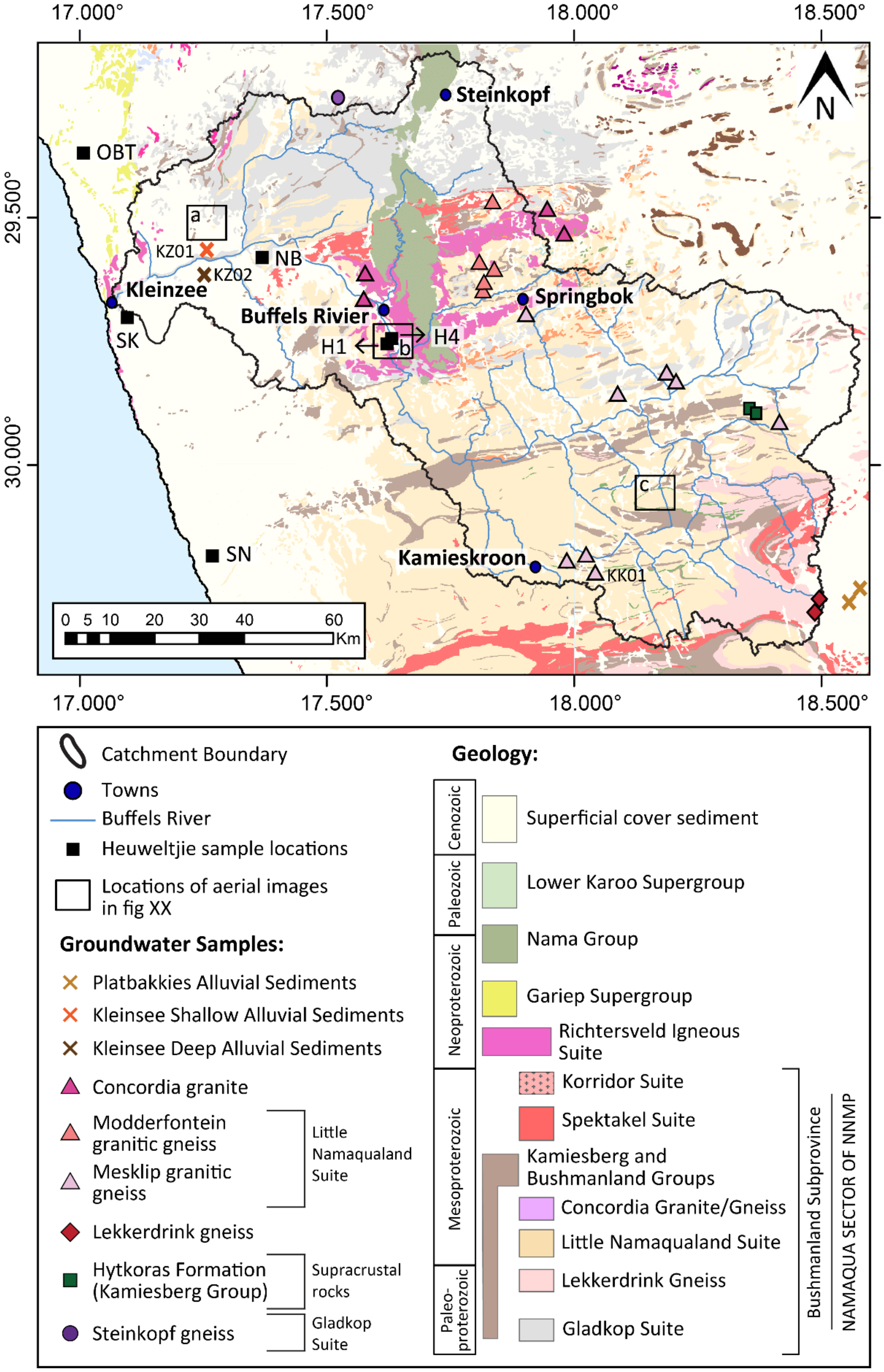

Figure 4. 2: Map of the geology of the area with the heuweltjie and groundwater sample locations. The symbology used to show the groundwater sample locations also show the aquifer host rock, refer to the legend. Heuweltjies marked as H1 and H4 refer to heuweltjie 1 and heuweltjie 4, respectively. The boxes marked a, b and c show the locations of the aerial images shown in Figure 4. 8.

4.3. Methods and Materials

4.3.1. Soils

For this study, the focus was to collect representative soil samples throughout the heuweltjie and interheuweltjie areas as well as in soils towards the west coast to analyse for radiocarbon. Samples included soils as well as carbonate nodules. Four samples were collected from various locations towards the west coast, around Nuttabooi, Koingnaas, Kleinsee and Oubeep (marked as NB, SN, SK and OBT, respectively in Figure 4. 2). These included heuweltjie sediments and carbonate nodules from other soil horizons (see Figure 4. 3). Two heuweltjies (marked as H1 and H4 in Figure 4. 2) in the Buffels River valley were identified and trenches was made through the heuweltjies by means of an excavator. The trenches were made in a T-shape with the longest trench in an east-west direction, starting in the interheuweltjie, extending across the heuweltjie, and ending in the interheuweltjie on the opposite end. The shorter trench was made from the interheuweltjie area along the south to the middle of the heuweltjie, intercepting the longer trench. The soil profiles were assessed and described before samples were collected. During the assessment of the soil profiles, each horizon was described according to the World Reference Base for Soil Resources, (2006) and horizon thicknesses were noted along with the presence of active and paleo termite nests. The full description of the heuweltjie profiles can be found in Francis et al (2021). The depths from the surface and the distance from the end of the trench of each sample location were noted. Upon return to Stellenbosch University, samples were dried in a temperature and humidity-controlled room for 48h before they were sieved through a 2mm soil sieve. Carbon nodules were collected were crushed by using a pestle and mortar to ensure that the sample is homogenous. Three subsamples of 10 g each were sent for further processing and analysis.

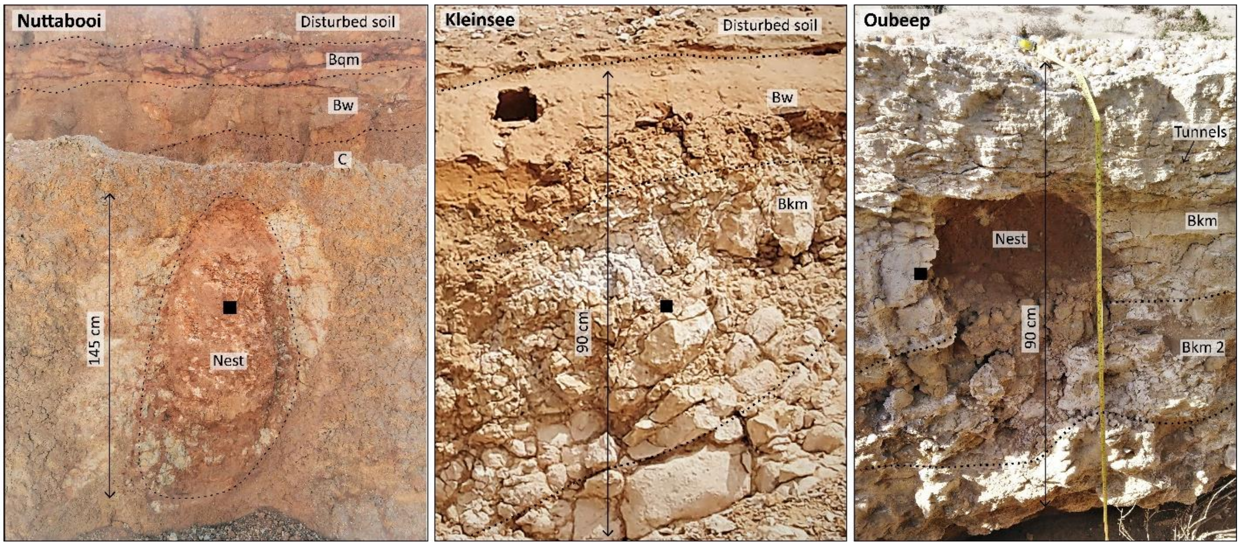

Figure 4. 3: Images showing the profiles sampled in Nuttabooi, Kleinsee and Oubeep, respectively. See (World Reference Base for Soil Resources, 2006) Guidelines for Soil Description. Bk: carbonate accumulation; Bkm: carbonate cementation; Bw: colour development; Bqm silica cementation

4.3.1.1. Radiocarbon in soils

Soil and carbon nodule samples were treated with 1 M HCl (Jull, 2006) and washed with distilled water until a neutral pH (4–5) was achieved and then dried. Samples were then placed in a two-finger flask with a special valve used to react the sample with phosphoric acid. Samples were placed in the standing finger and the phosphoric acid in the other. After closing the flask, the acid (85% H_3PO_4) was poured onto the sample to produce CO_2. The CO_2 produced from the carbonate in the sample was introduced into the in-line combustion/CO_2 purification system through the valve (Molnar, Janovics, Major, *et al.*, 2013). After purification, CO_2 gas was captured in a tube, the tube was sealed and sent for graphitization. All the AMS graphite targets were prepared by a sealed tube graphitization method (Rinyu, Orsovszki, Futó, *et al.*, 2015).

The ^{14}C measurements were performed from the graphite targets with a MICADAS accelerator mass spectrometer in the ICER laboratory. Fossil marble (IAEA-C1, 0.0 pMC) and known age travertine reference material (IAEA-C2, 41.14 pMC) were used a blank standard material and a control sample, respectively. This was done to determine if any modern/fossil carbon contamination is introduced during the extraction or graphitisation procedure. The overall measurement uncertainty for samples was < 3.0 ‰, including normalization, background subtraction, and counting statistics.

4.3.1.2. $\delta^{34}S$ SO_4^{2-} and $\delta^{18}O$ SO_4^{2-}

A total of 13 soil samples of 10 g each were washed with 20ml of 5% HCl to remove any carbonates. The supernatant was then filtered through a 0.45µm cellulose acetate filter into glass beaker. MiliQ water was added to the solution in the beaker to make up a solution of 150ml. $BaCl_2$ was added with a dropper and the solution was swirled and was set aside until a precipitate ($BaSO_4$) has formed and supernatant is clear. The supernatant was discarded, and the precipitate, containing the sulphate, was washed MiliQ water until pH was neutral. The precipitate was oven dried at 60°C for approximately 12 hours until it was completely dry. The dried samples were analysed for $\delta^{18}O$ SO_4 and $\delta^{34}S$ SO_4 using a DeltaPLUS XP stable isotope ratio mass spectrometer equipped with a Flash Isolink elemental analyser (Thermo Scientific). $\delta^{34}S$ SO_4^{2-} values are reported relative to the Vienna Canyon Diablo Troilite (VCDT) scale while the $\delta^{18}O$ SO_4^{2-} values are reported relative to VSMOW.

4.3.2. Groundwater

Groundwater anion data was obtained from van Gend et al., 2020 (Supplementary Table 2. 1, page 58), while the $\delta^{13}C$ CO_3 and $\delta^{18}O$ CO_3 data was obtained from Chapter 3. The sampling procedures described in the above-mentioned contributions were followed for the groundwater samples collected for this contribution.

4.3.2.1. Sample preparation for $\delta^{34}S$ SO_4^{2-} and $\delta^{18}O$ SO_4^{2-} in groundwater

A total of 16 groundwater samples were prepared and analysed. Each groundwater sample of 500ml was placed into a separatory funnel and 1mg of NaOH was added. The solution was mixed thoroughly before 5-7ml of BaCl2 was added to form a cloudy solution. It was set aside for the precipitate to accumulate at base of funnel. The wet precipitate was extracted into clean separation funnel and washed with MiliQ water. The washing process was repeated until a pH is of between 6 and 7 was reached. The samples were then frieze dried before the dried samples were analysed using the same equipment mentioned in section 3.1.3.

4.3.3. Heuweltjie carbonate age calculations

The ages (t) of inorganic carbonates (calcite/calcrete) are commonly calculated using the conventional decay equation.

$$t = \frac{5730}{\ln 2} \ln\left(\frac{A_0}{A}\right) \qquad \text{Equation 1}$$

where 5730 is the half-life of ^{14}C in years, A_0 is the initial ^{14}C activity, and A is the measured ^{14}C activity. This conventional radiocarbon age equation assumes that the activity of the ^{14}C isotope decreases as a function of radioactive decay only. However, in reality there are various processes that may affect the ^{14}C activity carbonates in soils.

4.3.3.1. Addition of old lithogenic carbonates

Inorganic carbonates in soils are either lithogenic in origin, hence directly derived from surrounding carbon rich rocks, or pedogenic in origin and formed in-situ as a result of the precipitation of dissolved inorganic carbon from water moving through the soils (Mikhailova, Bryant, Galbraith, *et al.*, 2018). Lithogenic carbonates could have variable ^{14}C activities or could be free of ^{14}C, causing dilution of the ^{14}C activities of the sample resulting inaccurate ages (Vogel & Geyh, 2008). In order to accurately determine the age of heuweltjies, the sample must be representative of carbonates that formed within the heuweltjies and hence free of lithogenic carbonates. Given that the geology of the Buffels River catchment is dominated by granitic gneisses and does not contain any carbonates, there are no lithogenic carbon in the soils of the Buffels River catchment. The geology of the region will therefore have no effect on the radiocarbon ages of the heuweltjie soils.

4.3.3.2. The reservoir effect

During precipitation of carbonates, the ^{14}C activity of the carbonate is in equilibrium with that of the atmospheric CO_2 at that instant. However, if groundwater is circulating through the soils, and carbonates are precipitating from the groundwater, the ^{14}C activity of the carbonate will be in equilibrium with the groundwater, which may or may not be in equilibrium with atmospheric CO_2 (Dal Sasso, Zerboni, Maritan, *et al.*, 2018; Geyh & Eitel, 1997). In the case where the groundwater is old and hence ^{14}C-depleted, the ^{14}C activity of the carbonate will reflect that of the groundwater and the age of the carbonate will be overestimated (Deutz, Montanez & Monger, 2002; Deutz, Montañez, Monger, *et al.*, 2001). This is often the case in areas where the groundwater levels are shallow and fluctuates regularly. For the purposes of this study, this factor can be ignored as the depth to the groundwater in the Buffels River catchment is deep and the heuweltjie carbonates are not affected by upward movement of groundwater.

4.3.3.3. Recrystallisation

Pedogenic carbonates often experience cycles of dissolution and recrystallisation when large amounts of water flushes through the soils. These events may occur often or over periods of thousands of years. When dissolution occurs, the carbonate is in contact with a “new” atmospheric CO_2 which is likely to be much different from the atmospheric CO_2 at the time of initial crystallisation. The system will then re-equilibrate and when the carbonate precipitates out again, the “new” atmospheric conditions will be captured (Dal Sasso *et al.*, 2018; Vogel & Geyh, 2008). However, in some cases, not all of the “old” carbonate is dissolved, and the “new” carbonate overprints the older carbonate, resulting in a carbonate sample with more than one age. Radiocarbon signatures will represent cycles of recrystallisation if overprinting has occurred or if complete dissolution and recrystallisation have occurred, it represents the last cycle of recrystallisation (Deutz *et al.*, 2002). For the purposes of this study, the challenges around recrystallisation was overcome by using very small and homogenous soil samples. Where nodules were analysed, the smallest and cleanest (based on visual inspection) was selected.

4.3.3.4. Soil organic matter and vegetation

Older ^{14}C depleted decaying organic matter in soils may be incorporated in the pedogenic carbonates, causing radiocarbon dilution, resulting in the soil carbonates to seem older than what they actually are (Deutz *et al.*, 2002). However, in arid regions, such as the Buffels River catchment, the residence time of soil organic matter is short (10 to 100 years) will therefore only cause an overestimation of up to 100 years (Potts *et al.*, 2009), which is not significant in terms of the ages of the carbonates in heuweltjies. Apart from decaying organic matter, living plants also have an effect on radiocarbon ages. When carbonates form, the ^{14}C of the carbonate is in equilibrium with the CO_2 of the soil gas which may or may not be in equilibrium with atmospheric ^{14}C activity. In vegetated areas, root respiration processes play a large role in controlling the CO_2 in soils causing the CO_2 of soil gas to differ from that of the atmosphere. When a carbonate is formed under these conditions, the initial ^{14}C activity may differ from that of the atmosphere at the time resulting in inaccurate ages. The isotopic signatures and hence ages of heuweltjie carbonates are unlikely to be affected by root respiration as the vegetation in the region is sparse. Moreover, due to the salinity of the soils, vegetation on heuweltjies is absent and the soils are aerated as a result of bioturbation. The CO_2 of soil gas in these aerated soils are in equilibrium with atmospheric CO_2 and ages calculated using the conventional decay equation is an accurate representation of the heuweltjie ages. The ages are reported in years before present (ybp) as these ages were not calibrated (Reimer, Bard, Bayliss, *et al.*, 2013) and 1σ errors are reported.

4.4. Results

4.4.1. Variation of groundwater chemistry over time

Anion concentrations in groundwater from van Gend et al., (2020) (Chapter 2, Supplementary Table 2. 1) are compared to the groundwater ages as calculated in Chapter 3 (Table 3. 3) and major variations are seen over time. There is an increase in the Cl^- concentration from 18 000 to 13 600 ybp (Figure 4. 4a). From here the Cl^- concentration decreases until 8 400 ybp where a slight increase is seen before it drops to the lowest concentration seen across the timeline at around 5 600 ybp after which the concentration increases slightly at 5 500 ybp. From there, the overall Cl^- concentration continues to decrease but there are large spikes in the Cl^- concentration at around 2 000 ybp and 600 ybp. Sulphate$^-$ and HCO_3^- follow a similar trend but their concentrations are much lower. The magnitude of the SO_4^{2-} changes is greater than that of HCO_3^- , which remains slightly more consistent over time. An increase in concentration of specifically sulphate around 8 000 ybp and between 5 600 and 5 500 ybp is also seen.

Groundwater $\delta^{18}O$ H_2O and δ^2H H_2O data from van Gend et al., (2020) (Chapter 2, Supplementary Table 2. 2) and $\delta^{13}C$ CO_3^{2-} and $\delta^{18}O$ CO_3^{2-} data (Chapter 3, Table 3. 1) is plotted with groundwater $\delta^{34}S$ SO_4^{2-} and $\delta^{18}O$ SO_4^{2-} data against groundwater ages calculated in Chapter 3 and these stable isotopes values in groundwater also vary through time (Figure 4. 4b and c). $\delta^{13}C$ CO_3^{2-} and $\delta^{18}O$ CO_3^{2-} as well as $\delta^{18}O$ H_2O and δ^2H H_2O values. Although $\delta^{13}C$ CO_3^{2-} and $\delta^{18}O$ CO_3^{2-} and do not react in the same way, changes are seen at 5 600 to 5 500 ybp, 2 000 ybp and 600 ybp which are consistent with the timing of changes that occurred in the ion concentrations. The $\delta^{18}O$ H_2O of groundwater is more stable over time than the δ^2H H_2O (Figure 4. 4 c). The increases seen in both are consistent with the changes in $\delta^{13}C$ CO_3^{2-} and $\delta^{18}O$ CO_3^{2-} and $\delta^{34}S$ SO_4^{2-} and $\delta^{18}O$ SO_4^{2-} isotopes (Figure 4. 4 b) as well as the changes in groundwater chemistry (Figure 4. 4 a) with time. The positive excursions occur at around 9 600 ybp, 8 000 ybp, 5 500 ybp, 2 000 and around 600 ybp. In all these periods, both $\delta^{18}O$ and δ^2H become more positive and hence are enriched in the heavy isotopes. In the case of the negative excursions at 8 400 ybp, 5 600 ybp and 3 800 ybp, both $\delta^{18}O$ and δ^2H signatures become more negative and therefore depleted in the heavy isotopes or enriched in the light isotopes. These negative excursions are also seen in the anion concentrations at the same time (Figure 4. 4 a) as well as in the $\delta^{13}C$ CO_3^{2-}, $\delta^{18}O$ CO_3^{2-}, $\delta^{34}S$ SO_4^{2-} and $\delta^{18}O$ SO_4^{2-}. At 5 600 ybp, where the ion concentrations are the lowest, $\delta^{13}C$ CO_3^{2-} and $\delta^{34}S$ SO_4^{2-} values are also at their lowest but the decrease is not as large for the $\delta^{18}O$ CO_3^{2-} and δ^2H values. The $\delta^{18}O$ SO_4^{2-} value for this specific sample was not obtained.

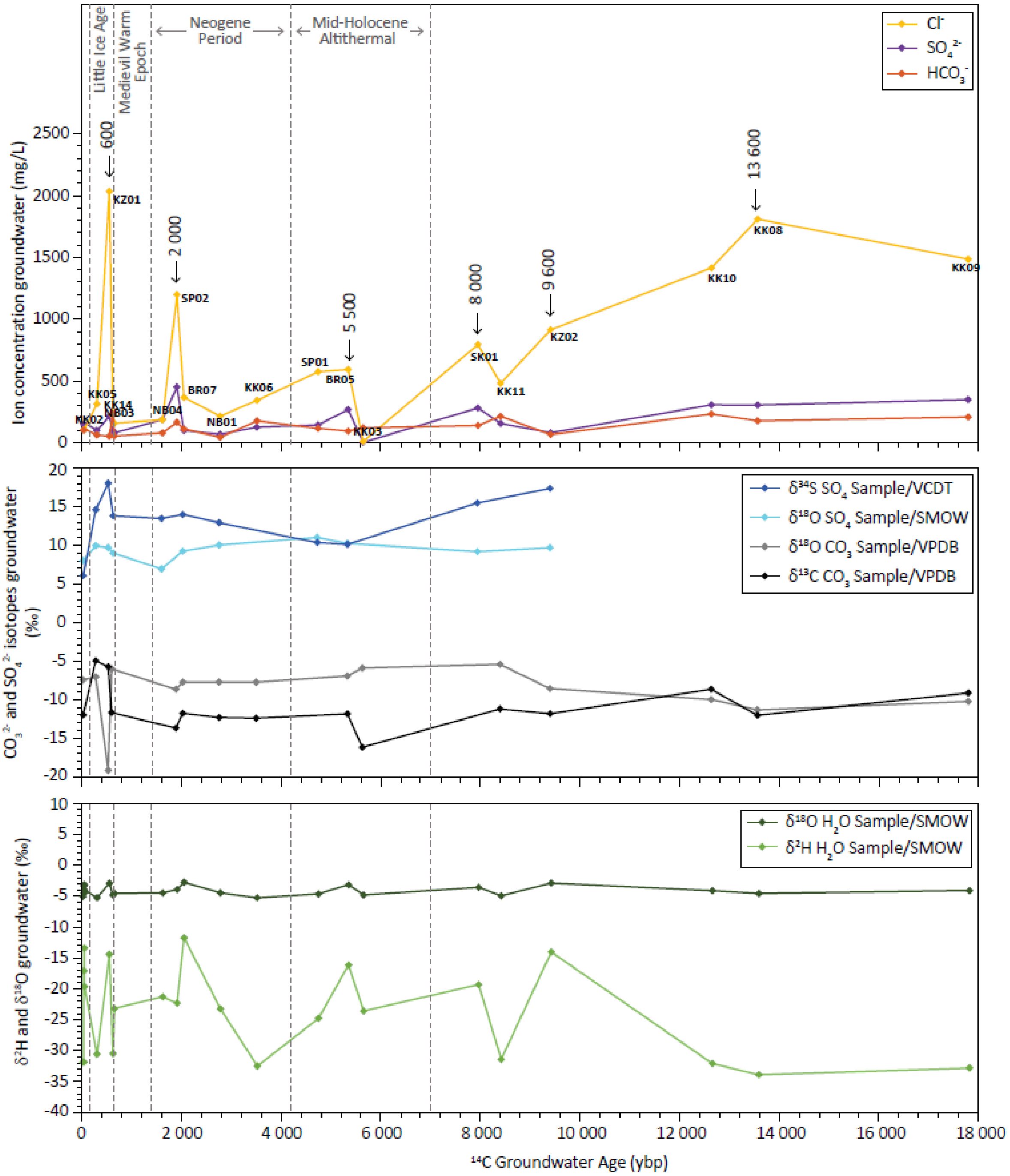

Figure 4. 4: Anion concentrations in groundwater and stable isotopes in groundwater from the Buffels River catchment plotted against ages. Groundwater ages as calculated in Chapter 3 (Table 3. 3). Previous known climatic periods are from Dewar and Stewart, 2017. a) anion concentrations over time indicating major salt input events in the past 18 000 years. b) variation in stable isotopes of CO_3 and SO_4^{2-} over the past 18 000 years. c) variation in stable isotopes of H_2O in groundwater for the samples dating up to 18 000 years old.

4.4.2. Soil carbonate ages

The ages of the soil carbonate from different areas within two heuweltjies in the Buffels River valley are shown in Figure 4. 5 and Figure 4. 6 and in Table 4. 1. The samples collected from Heuweltjie 4 contained less carbonates than Heuweltjie 1 and only four carbonate ages were obtained compared to 13 ages that were obtained for Heuweltjie 1. In both heuweltjies the ages of the carbonates generally increase with depth. The carbonates reach a maximum age of 30 500 ± 171 ybp in Heuweltjie 1 at 110 cm depth and 30 500 ± 171 ybp at the same depth in Heuweltjie 4 (Table 4. 1). The youngest carbonates have ages of 2 790 ± 29 ybp and 3 050 ± 41 ybp for Heuweltjie 1 and Heuweltjie 4 respectively and are located at a depth of 10 cm in both heuweltjies. The carbonates in the center of the heuweltjie are situated much deeper than similar-aged carbonates towards the edges, resulting in a U-shaped curve describing the depth to carbonates of similar age in Heuweltjie 1 (Table 4. 1 and Figure 4. 5). The ages of the oldest heuweltjie carbonates are consistent with other older pedogenic carbonates from the samples collected towards the west coast with ages of up to 33 300 ± 224 ybp. Of the four samples sampled towards the west coast, the youngest carbonates were dated to be from 16 410 ± 62 ybp (Table 4. 1). This sample was collected from Koingnaas (SN30-5) which is the furthest south along the coast. The age of the sample collected from Kleinsee is 25 900 ± 145 ybp which is comparable to the age of the oldest U-shaped curve seen in heuweltjie 1 (Table 4. 1 and Figure 4. 5). The two remaining samples from Nuttabooi (NB1-F) and Oubeep (OBT358-2A-40) are the oldest and is comparable to the oldest samples from heuweltjie 1 (Table 4. 1).

Table 4. 1: Radiocarbon activity and calculated ages of calcite in heuweltjie soils

Sample ID	**Depth (cm bgl)**	**pMC**	**pMC unc. (1σ)**	**Radiocarbon age ± 1σ error**
West Coast Samples				
NB1-F	200	1.99	0.06	32400 ± 234
SK4-F	80	4.34	0.08	25900 ± 145
SN30-5	40	13.73	0.10	16410 ± 62
OB358-2A-40	40	1.78	0.05	33300 ± 224
Heuweltjie 1				
H1-2-10	10	71.35	0.25	2790 ± 29
H1-13-50	50	32.02	0.13	9410 ± 33
H1-13-60	60	5.39	0.07	24100 ± 109
H1-13-110	110	2.49	0.05	30500 ± 171
H1-24-140	140	15.59	0.10	15360 ± 52
H1-24-230 (nest)	230	4.00	0.05	26600 ± 108
H1-24-240 (base of nest)	240	30.73	0.21	9750 ± 56
H1-25-90	90	31.11	0.16	9650 ± 43
H1-25-160 (nest filling)	160	65.40	0.20	3510 ± 26
H1-25-160 (nest carapace)	160	63.95	0.20	3690 ± 26
H1-25-190 (base of nest)	190	31.37	0.19	9580 ± 49
H1-39-40	40	28.86	0.15	10270 ± 44
H1-40-70	70	6.26	0.08	22900 ± 103
Heuweltjie 4				
H4-19-10	10	69.12	0.34	3050 ± 41
H4-19-110	110	1.38	0.03	35400 ± 192
H4-41-70	70	20.04	0.12	13290 ± 48
H4-42-110 (nest)	110	1.64	0.03	33900 ± 171

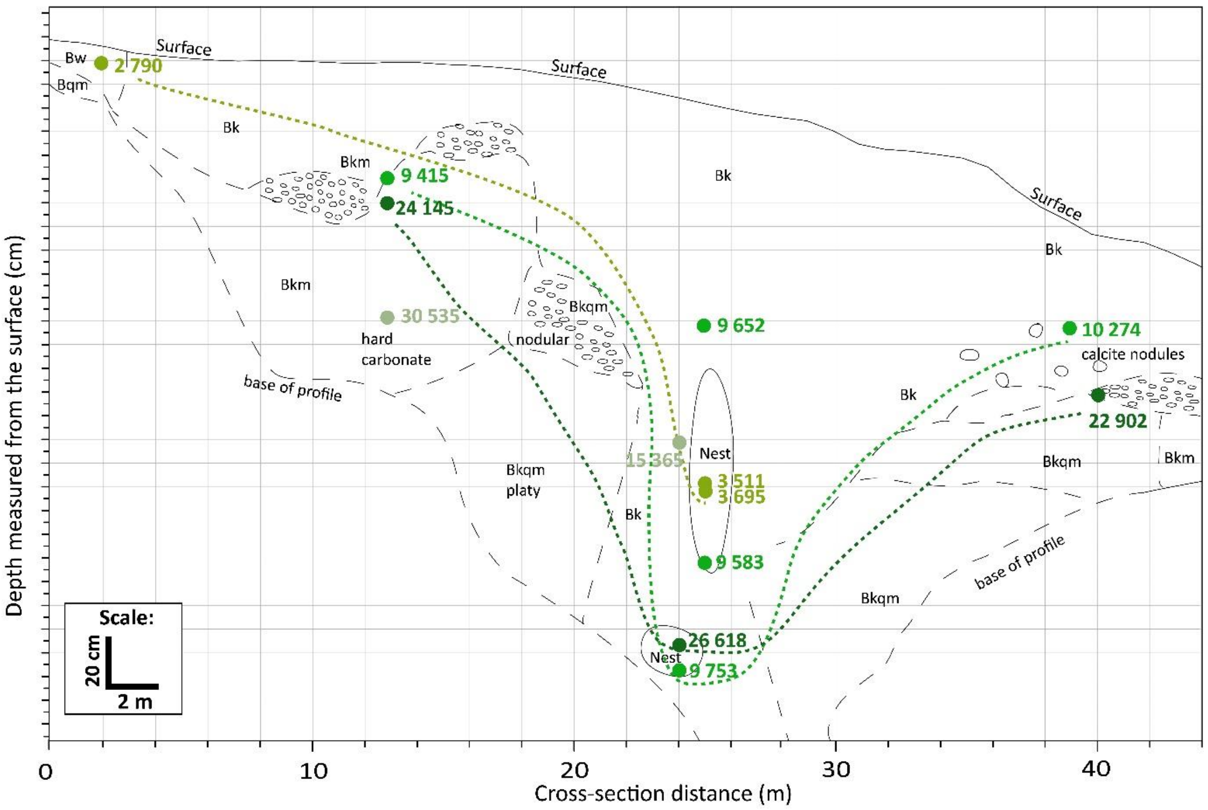

Figure 4. 5: Cross-section of heuweltjie 1 showing the distribution of radiocarbon ages for carbonates in the heuweltjie in green. The dotted green lines in different shades of green indicate the depth to calcite of similar ages. Bk = carbonate accumulation; Bw = development of colour and structure; Bkm = carbonate cementation; Bqm = silica cementation; Bkqm = carbonate and silica cementation (World Reference Base for Soil Resources, 2006).

4.4.3. $\delta^{18}O$ and $\delta^{34}S$ values from SO_4^{2-} in heuweltjie soil and groundwater

The samples collected from Heuweltjie 1 contained too little sulphate for $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$ to be determined. Heuweltjie 4 contained sulphates in the form of gypsum, in some places in sufficient quantity to be classified as a gypsic soil horizon (Figure 4. 6). The $\delta^{34}S\ SO_4^{2-}$ values are relatively consistent ranging between 17.1 and 18.7 ‰ while the $\delta^{18}O\ SO_4^{2-}$ are slightly more variable between 8.3 and 11.4 ‰ (Table 4. 2 and Figure 4. 6). There is no correlation ($R^2 = 0.01$) between lateral distance or depth and changes in the $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$ values. The $\delta^{18}O\ SO_4^{2-}$ values of the heuweltjies (Figure 4. 6) are comparable to that of the groundwater and range between 8.3 and 11.4 ‰ with a mean of 9.4 ‰. For the groundwater samples, these values range between 7.0 and 12.0 ‰ with a mean value of 9.5 ‰. In contrast, the $\delta^{34}S\ SO_4^{2-}$ values of the samples collected from the heuweltjies are very different from that of the groundwater. $\delta^{34}S\ SO_4^{2-}$ in heuweltjie soils range between 17.1 and 18.6 ‰ whereas that of the groundwater is much more variable, ranging between 9.0 and 18.0 ‰

with 1 outlier of 6.0 ‰ (Table 4. 2). However, there are three groundwater samples for which both the $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$ are in the same range as that of the heuweltjies.

Table 4. 2: $\delta^{34}S\ SO_4$ and $\delta^{18}O\ SO_4$ data for sulphates in groundwater and in heuweltjie soils

Sample ID	**$\delta^{34}S\ SO_4$ sample/VCDT**	**$\delta^{18}O\ SO_4$ sample/SMOW**
Heuweltjies		
H4-19-60	17.45	9.03
H4-19-110	17.51	8.75
H4-19-110 (nest)	17.55	8.28
H4-32-80	17.83	11.42
H4-32-100	18.02	10.34
H4-32-130	17.95	10.14
H4-19-160	17.07	8.58
H4-22-60	17.97	8.79
H4-22-120	18.05	9.68
H4-22-160	18.17	8.56
H4-38-70	18.56	9.52
H4-38-100	18.48	9.83
H4-38-130	18.67	9.40
Groundwater		
BR05	10.1	10.2
BR07	14.0	9.2
CD02	6.1	8.0
CD03	15.0	9.6
KK01	17.9	11.1
KK02	11.8	8.4
SP01	10.4	11.0
KK04	14.4	9.4
KK05	14.6	9.9
KZ01	18.0	9.7
KZ02	17.4	9.7
NB01	12.9	10.0
NB02	9.0	12.0
NB03	13.5	9.0
NB04	13.8	7.0
SK01	15.5	9.2

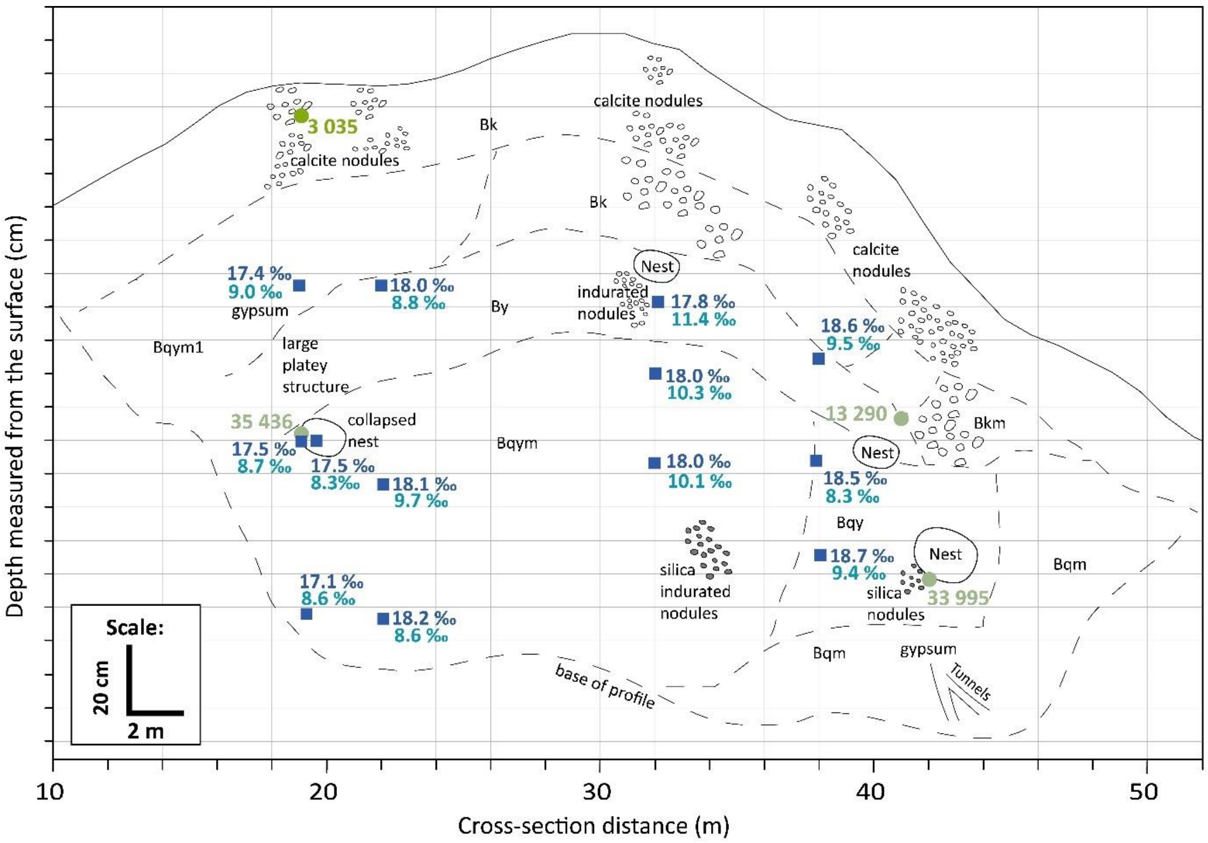

Figure 4. 6: Cross-section of heuweltjie 4 showing the distribution of radiocarbon ages for carbonates in the heuweltjie in green. The sediment sample locations for δ^{34}S SO_4^{2-} and δ^{18}O SO_4^{2-} are indicated by the blue squares. δ^{34}S SO_4^{2-} values are shown in darker blue while δ^{18}O SO_4^{2-} values are shown in lighter blue. **δ^{34}S** SO_4^{2-} **values are reported relative to the** VCDT scale while the δ^{18}O SO_4^{2-} values are reported relative to VSMOW. Bk = carbonate accumulation; Bkm = carbonate cementation; By = gypsum accumulation; Bqm = silica cementation; Bqym = gypsum and silica cementation (World Reference Base for Soil Resources, 2006).

4.5. Discussion

4.5.1. Heuweltjies and Saline Groundwater

4.5.1.1. Changes in groundwater chemistry over time

Chloride is often used as a tracer in groundwater and soil studies because it does not readily enter oxidation or reduction reactions and does not form soluble complexes with other ions. Moreover, Cl is not commonly adsorbed to surfaces and it remains in solution over the largest concentration range (Bouchaou *et al.*, 2008; Huang, Pang, Liu, *et al.*, 2017). In the Buffels River valley, gypsum and calcite are significant secondary mineral components in the heuweltjie soils (Figure 4. 5 and Figure 4. 6) where they form gypsic, calcic and petrocalcic horizons (IUSS Working Group WRB, 2015). Here, the groundwater SO_4^{2-} and HCO_3^- are second and third in abundance, respectively, after Cl^- (Figure 4. 4a). During episodes of leaching, Cl^- (halite log K = 1.59, Chase, 1998) is readily flushed into the groundwater system. This would be followed by SO_4^{2} during higher intensity leaching events (log K gypsum = -4.61, Garvin et al., 1987) and only with the highest leaching volumes is HCO_3^- expected to be flushed into the system as $CaCO_3$ present in the profile, dissolves (log K calcite = -8.48, Plummer and Busenberg, 1982). The variation in the anion concentrations in the groundwater can therefore be related to the intensity of recharge events over time in the Buffels Rivers soil-groundwater system. This is seen in Figure 4. 4a where Cl^- is most concentrated in the groundwater followed by SO_4^{2-} and HCO_3^- for each event age. It is also clear that the magnitude of the Cl^- increase is greater than that of changes in SO_4^{2-} which is in turn greater than that of HCO_3^- (Figure 4. 4a). By looking at these anion concentrations over time, a robust timeline of events is evident. Apart from the major anions in the groundwater, the stable isotope data of the groundwater also shows significant peaks which can be related to these salt flushing periods. $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$ as well as $\delta^{13}C\ CO_3^{2-}$ and $\delta^{18}O\ CO_3^{2-}$ in groundwater shows distinct changes around 5500 ybp, 2000 ybp and 600 ybp. In the case of $\delta^{18}O\ SO_4^{2-}$, a smaller peak is seen around 2000 ybp while the larger peak is seen around 600 ybp (Figure 4. 4b). Events seen in the groundwater chemistry around 5500 ybp correspond to the Mid-Holocene Altithermal, while that occurring around 2000 ybp correspond to the end of the Neogene period. The events that occurred 600 years ago correspond to the early Little Ice Age. Between 1600 ybp and 600 ybp, no significant events are noticed. The Medieval Warm Epoch prevailed during this period as a result, it was to warm and dry for salts to be flushed into the groundwater system.

4.5.1.2. Sulphates and salts in soils and groundwater

The combination of δ^{34}S SO_4^{2-} and δ^{18}O SO_4^{2-} in natural systems provides valuable information regarding the origin of sulphates and hence other salts, as well as the processes that have occurred in natural systems (Balci, Mayer, Shanks, *et al.*, 2012; Balci, Shanks, Mayer, *et al.*, 2007; Miljević, Boreli-Zdravković, Veličković, *et al.*, 2013; Tichomirowa, Heidel, Junghans, *et al.*, 2010). The advantage of using both δ^{34}S SO_4^{2-} and δ^{18}O SO_4^{2-} isotopes is that these values are not necessarily affected in the same way during natural processes. The isotope signatures of oxygen in SO_4^{2-} can be used to understand the mechanism of sulphate formation as there are two sources of oxygen, atmospheric oxygen and oxygen in meteoric water and the δ^{18}O signature of these sources are very different (Mayer, Fritz, Prietzel, *et al.*, 1995). Atmospheric oxygen has a δ^{18}O of 23.5 ‰ while the δ^{18}O value of meteoric water is typically less than 0 ‰ but oxygen derived from both the atmosphere and water can be incorporated in sulphate in various ratios depending on the reaction pathway (Balci *et al.*, 2007; Claypool, Holser, Kaplan, *et al.*, 1980). However, once in solution, the δ^{18}O SO_4^{2-} is not affected by exchange reactions with silicate minerals, but exchange of ^{18}O-^{16}O between sulfate and water could occur, but only in low pH environments and long residence times (Nordstrom, Wright, Mast, *et al.*, 2007). Therefore, δ^{18}O SO_4^{2-} in groundwater in the Buffels River catchment will remain the same as that of the source, as the groundwater pH is close to neutral (between pH 6 and 8, (van Gend *et al.*, 2020)). The δ^{18}O SO_4^{2-} signatures of heuweltjies (8.3 to 11.4 ‰) are comparable to δ^{18}O SO_4^{2-} to the δ^{18}O SO_4^{2-} of the groundwater (7.0 to 12.0 ‰), proving that the sulphates in heuweltjies and in the groundwater have undergone the same mechanism of formation. Moreover, the fact that these sulphates have the same mechanism of formation confirms that the sulphates must be of similar origin which can be constrained by their δ^{18}O SO_4^{2-} signatures.

The δ^{34}S SO_4^{2-} signature for evaporites such as gypsum ranges between 10 ‰ and 30 ‰, with an average of 16 ‰, while the present day δ^{18}O SO_4^{2-} and δ^{34}S SO_4^{2-} signature in ocean water is 7.6 ‰ to 9‰ and 20.1 ‰, respectively (Bottrell & Newton, 2006; Osselin, Saad, Nightingale, *et al.*, 2019; Rivas, Pozo & Paz, 2014). The δ^{34}S SO_4^{2-} signatures of aerosols, evaporites or the ocean water from the Buffels River catchment is unknown, but data from a study done in an area between 360 and 760 km north of the Buffels River catchment indicated the following: 1) seawater collected from Swakopmund showed δ^{34}S SO_4^{2-} of 20.3 ‰; 2) the δ^{34}S SO_4^{2-} for an aerosol sample collected near the coast at Swakopmund is 15.9 ‰ ;; and 3) atmospheric non sea salt has a δ^{34}S SO_4^{2-} value of 15.6 ± 3.1 ‰ (Eckardt & Spiro, 1999). Apart from a slightly different geological regime, the climatic and environmental conditions of this region is very similar to that of the Buffels River catchment and it is plausible to use these values as reference values to compare to the Buffels River catchment.

In a previous study done in the Buffels River catchment, it was suggested that the main source of salts in the Buffels River catchment is dry deposition of marine aerosols (van Gend *et al.*, 2020). In order to evaluate the contribution of marine aerosols to the salts in the groundwater system, the relationship between Cl^- and SO_4^{2-} together with the relationship between the $\delta^{34}S$ SO_4^{2-} and the $Cl^-:SO_4^{2-}$ ratios of groundwater and sediment samples should be evaluated. Seawater generally has a $Cl^-:SO_4^{2-}$ ratio of 1:10 which is very close to the reference value of 1:10.1 from the sample collected at Swakopmund (Eckardt & Spiro, 1999). When comparing the groundwater and heuweltjie data to this reference value, the groundwater samples collected from granitic gneiss host rocks display SO_4^{2-} enrichment relative to the seawater sample, while SO_4^{2-} in groundwater samples collected from the sediments where the heuweltjie density is high, is depleted in relation to seawater (Figure 4. 7). Moreover, the heuweltjie sediment samples are enriched in SO_4^{2-} (Figure 4. 7), while the aerosol sample collected from Swakopmund is also enriched in SO_4^{2-} relative to seawater. Aerosols are a combination of salts from sea-spray and atmospheric non-sea-salts (NSS) and in this case the aerosol is enriched in SO_4^{2-} relative to the seawater, suggesting that there is an atmospheric aerosol component with higher SO_4^{2-} concentration.

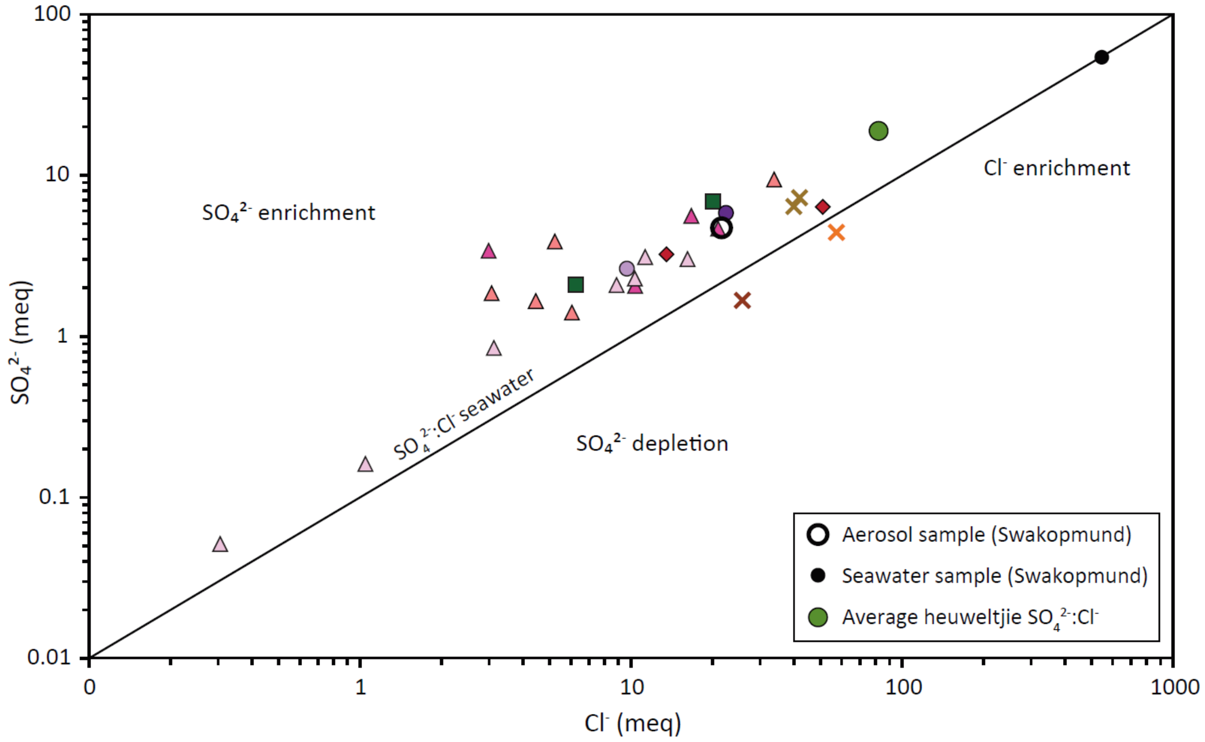

Figure 4. 7: The relationship between SO_4^{2-} and Cl^- in groundwater from the Buffels River catchment, heuweltjie sediments from the Buffels River catchment and an aerosol and seawater sample both from Swakopmund. The aerosol and seawater data is used as reference values and was taken from Eckardt & Spiro, (1999). See the Figure 4. 2 for an explanation of the symbology used for the groundwater samples.

The Cl^-:SO_4^{2-} ratio compared to the $\delta^{34}S\ SO_4^{2-}$ provides further insight into the origin of the sulphates and hence other salts (Eckardt & Spiro, 1999). The $\delta^{34}S\ SO_4^{2-}$ of the heuweltjie sediments plot in the upper NSS field, just below the line representing the seawater $\delta^{34}S\ SO_4^{2-}$, indicating that the origin of sulphates in the heuweltjie sediments are a combination of marine salts and NSS. The $\delta^{34}S\ SO_4^{2-}$ of the groundwater is more variable but can be related to the geology and the spatial distribution of heuweltjies. Groundwater samples collected from the sediments where the heuweltjie density is high (Figure 4. 8) has the similar $\delta^{34}S\ SO_4^{2-}$ signatures than that of the heuweltjie soils but are depleted in SO_4^{2-} relative to seawater while the heuweltjies are enriched in SO_4^{2-} relative to the seawater (Figure 4. 9). This can be explained by the fact that heuweltjies consist of nutrient rich soils (Francis & Poch, 2019; McAuliffe, Hoffman, McFadden, Bell, *et al.*, 2019; McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Midgley & Musil, 1990) and are zones where salts are being accumulated. When water passes through the heuweltjies, the more soluble salts, NaCl, will be dissolved first and transported downwards into the groundwater, leaving the heuweltjie material depleted in Cl^- and hence SO_4^{2-} enriched. Sulphates, are less soluble and will remain in the heuweltjies, explaining the Cl^- enrichment and SO_4^{2-} depletion in the groundwater (Figure 4. 9). The small amount of sulphates that are dissolved and transported into the groundwater have the same $\delta^{34}S\ SO_4^{2-}$ signature than that of the heuweltjies, indicating that the heuweltjie salts are flushed into the groundwater system.

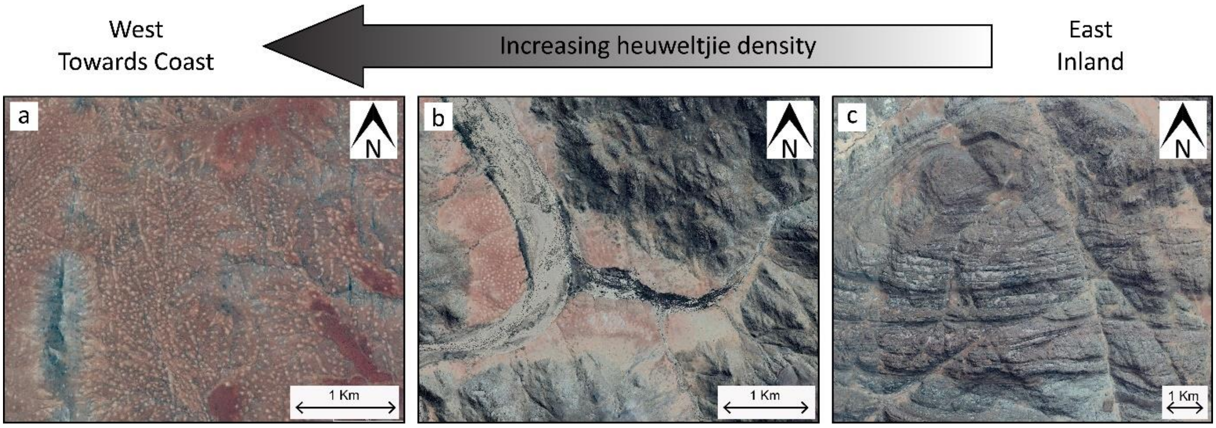

Figure 4. 8: Aerial images showing the increase in heuweltjie density from towards the west of the Buffels River catchment. The abundance of granitic gneisses towards the east of the catchment is also shown. The location of the images relative to the catchment boundaries are shown in Figure 4. 2 as outlined boxes marked a, b and c.

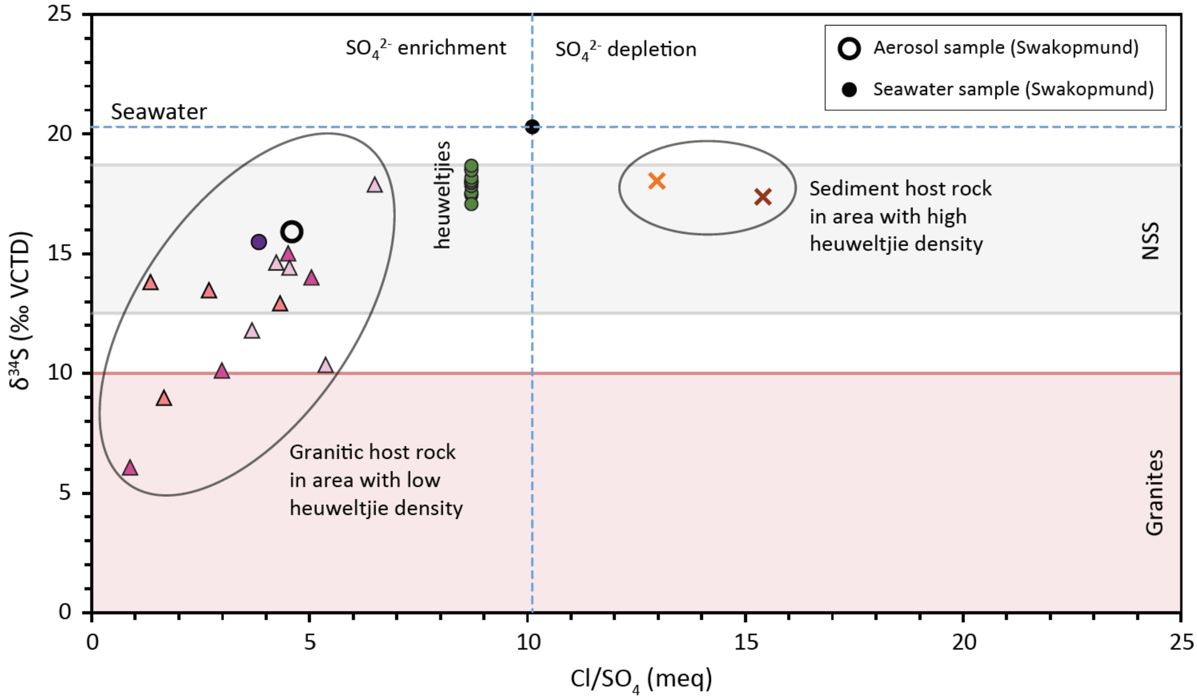

Figure 4. 9: $\delta^{34}S\ SO_4^{2-}$ compared to the Cl/SO4 ratio for groundwater and heuweltjie samples. The reference $\delta^{34}S$ values for granites, seawater, aerosols and NSS are also shown (Claypool *et al.*, 1980; Eckardt & Spiro, 1999; Hoefs, 2015). See the Figure 4. 2 for an explanation of the symbology used for the groundwater samples

In contrast, groundwater samples collected from granitic gneiss host rocks where heuweltjie density is low are enriched in SO_4^{2-} relative to seawater and heuweltjies and the $\delta^{34}S\ SO_4^{2-}$ signature is different from that of the heuweltjies soils (Figure 4. 9 and Figure 4. 8). Instead, the $\delta^{34}S\ SO_4^{2-}$ signature of the groundwater from granitic gneiss host rocks plot between that of the aerosol sample and the granite $\delta^{34}S\ SO_4^{2-}$ signature field. Keeping in mind that the $\delta^{18}O\ SO_4^{2-}$ signature of the groundwater and heuweltjie samples are so similar, indicating the mechanism of formation, the origin of the sulphates in the groundwater hosted in granitic gneiss rocks are also a combination of NSS and marine salts transported as aerosols. However, here, the sulphates and other salts are transported directly into the granitic gneiss host rock aquifer during recharge as there are no heuweltjies present where some of the salts are stored. The $\delta^{34}S$ signature of granitic rocks are between 0 and 10 ‰ (Hoefs, 2015), and once in the aquifer, the $\delta^{34}S\ SO_4^{2-}$ signature is then affected by the $\delta^{34}S$ of the granitic gneisses, causing the deviation from the original of the aerosol. This “granitic gneiss”-influence is not seen in the sediment-hosted groundwater or in the heuweltjie sediments suggesting that it is confined only to the fractured rock aquifer system. The contribution of $\delta^{34}S$ from granitic gneiss caused a decrease in the overall $\delta^{34}S\ SO_4^{2-}$ of the groundwater. The effect of the water-rock interaction between groundwater and the granitic gneisses is further shown in Figure 4. 10 where $^{87}Sr/^{86}Sr$ in groundwater is compared to the δ^{34}S SO_4^{2-} in groundwater across the catchment. $^{87}Sr/^{86}Sr$ values in groundwater provides an indication of the degree of water rock interaction (Cartwright, Weaver & Petrides, 2007; Négrel & Petelet-Giraud, 2005), specifically in a granitic environment such as the Buffels River catchment. The granitic gneisses in this region are highly radiogenic (Macey *et al.*, 2018) and groundwater interacting with these granitic host rocks have high $^{87}Sr/^{86}Sr$ ratios that has been related to the $^{87}Sr/^{86}Sr$ signature of the host rock (van Gend *et al.*, 2020). Groundwater hosted in the sediments have much lower $^{87}Sr/^{86}Sr$ signatures, while groundwater hosted in the granitic rocks have elevated $^{87}Sr/^{86}Sr$ signatures which reflects the $^{87}Sr/^{86}Sr$ signatures of the highly radiogenic granitic rocks in the region.

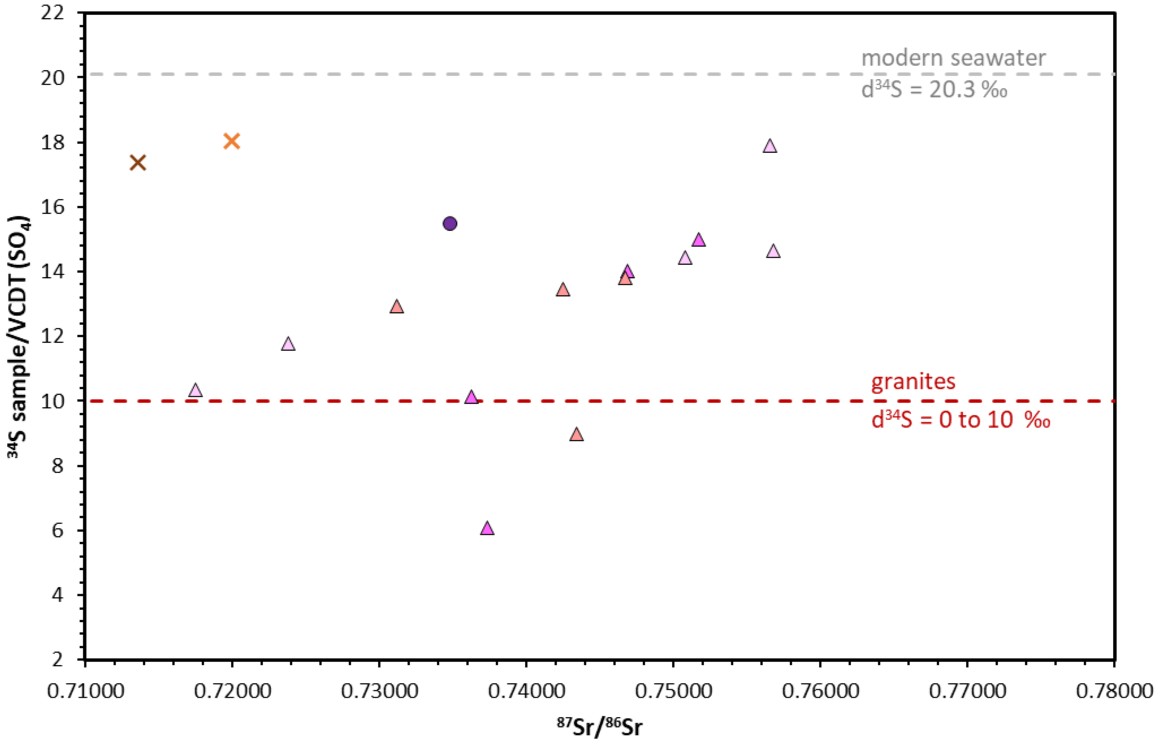

Figure 4. 10: Relationship between $^{87}Sr/^{86}Sr$ and δ^{34}S SO_4^{2-} values for groundwater samples marked according to the host rock geology. See the Figure 4. 2 for an explanation of the symbology used for the groundwater samples. The reference δ^{34}S SO_4^{2-} values for gypsum as well as the reference δ^{34}S values for granites and seawater are also shown (Claypool *et al.*, 1980; Eckardt & Spiro, 1999; Hoefs, 2015) .

4.5.2. *Infiltration processes through heuweltjie over time*

Calcite horizons present in heuweltjies represent continuous wetting and drying events causing cycles of calcite dissolution and recrystallisation (Francis & Poch, 2019). When calcite crystallizes, the carbon atom is in isotopic equilibrium with the atmospheric CO_2 at the time that it is formed (Dal Sasso *et al.*, 2018). However, when calcite is dissolved and recrystallized, its isotopic signature is reset to be in equilibrium with the atmospheric conditions at the time of recrystallisation. As a result, the age of the crystallisation event is recorded in the calcite and not the actual age of the carbon (Dal Sasso *et al.*, 2018). Heuweltjie carbonates have been dated previously and ages of between 18 770 and 31 290 ybp have been noted (Potts *et al.*, 2009). However, carbonates in heuweltjies have never been related to specific periods of high infiltration in the past.

The depth to the carbonate horizon in calcareous soils is proportional to the mean annual precipitation (MAP) (Zamanian, Pustovoytov & Kuzyakov, 2016). The depth to the calcite-bearing horizons of a similar age in the heuweltjies therefore indicate the MAP where events of increased soil leaching took place for a given calcite age, and so would provide an indication of a wetting front that travelled through the soil profile. In Heuweltjie 1, there are three U-shaped wetting fronts formed by the ages of the carbonate nodules (Figure 4. 5): 2700 and 3000 ybp, 9700-9400 ybp, and >24 000 ybp, with the shallowest calcite generally being younger. These periods correspond to the ages of increased salinity in the groundwater and also to the periods of increases in the $\delta^{18}O$ H_2O and $\delta^{2}H$ H_2O in the groundwater (Figure 4. 4c). The increase in the $\delta^{18}O$ H_2O and $\delta^{2}H$ H_2O signature of the groundwater around 9600 ybp and the sharp increase just before 2000 ybp both indicate an increase in the humidity which suggests an overall wetter period (Hoefs, 2015).

The U-shaped front clearly shows that water is preferentially transported through the middle of the heuweltjie as carbonates situated deeper in the center of the heuweltjie are the same age as those at shallower depths along the edges of the heuweltjie. This shows that the carbonates in the centre of the heuweltjie around the nest have been leached to a greater depth than those at the edges. The center of the heuweltjie above the nest area is heavily bioturbated, with many tunnels and macropores. Heuweltjie 4 lacks a significant moisture front, but Heuweltjie 4 also does not host a large termite nest where termites have reworked the sediments and constructed tunnels as they built their nests. This indicates that heuweltjies and more specifically termite activity plays a role in facilitating infiltration of surface water, and facilitating groundwater recharge especially during specific, episodic, large volume leaching events. It was always thought that termite nests or mounds are known to shed water rather than facilitate the downwards funnelling of water (Turner, 2006). This study indicated that heuweltjies, *Microhodotermes viator* nests, behave completely differently than other species in the Hodotermitidae family. This is novel this is in terms of the understanding of water movement in termite affected soils. Given that heuweltjies cover up to 25 % of the surface of south western Africa (Lovegrove & Siegfried, 1986), the role that specific species of termites play in water movement within soils should be reconsidered.

4.5.3. Implications of recharge patterns and saline groundwater

The history of human occupation in Namaqualand is strongly tied to periods of increased rainfall, whereas the dry periods are mainly represented in the archaeological record by isolated human burials (Dewar & Stewart, 2017). Namaqualand is currently experiencing arid conditions and although the modern population in Namaqualand has not decreased as it would have in the past, the current arid conditions has led to an increase in the groundwater usage in the region (Abiye, 2016). Many communities are dependent on groundwater as their only supply of potable water, but the groundwater in the region is variably saline (van Gend *et al.*, 2020). In addition to this, one of the main economic sectors in Namaqualand, agriculture in the form of pastoralism, also relies on groundwater as the main source of potable water. In the past, the natural vegetation was sufficient feed for the livestock. However, in the current climatic conditions, farmers must provide additional feed to livestock and many farmers have started to cultivate portions of their land to provide their livestock with feed, increasing the dependence on groundwater for irrigation.

The water resources in Namaqualand are already stressed but with future climate predictions, the population is likely to become even more dependent on groundwater resources. According to Beal et al., (2011), Biastoch et al., (2009) and Weldeab et al., (2013), climate change will cause a poleward shift of the austral mid-latitude westerlies and weakening of the southern Benguela upwelling system allowing increased leakage of warm Agulhus waters. These authors note that climatic shifts will not only decrease precipitation in the winter rainfall zone but will cause an increase in sea surface temperature along the coast and therefore a likely reduction in coastal fog formation. In addition to this, it is predicted that Namaqualand will experience increasing spring and autumn evapotranspiration in the coastal areas (Davis *et al.*, 2016; MacKellar *et al.*, 2007). During these drier periods, amount of recharge will decrease and although the recharge is necessary for the sustainability of the groundwater system, the groundwater will not become more saline if salts can't be flushed into the system. This study has highlighted the complexities of groundwater recharge. During the wetter periods of much-needed recharge, salts are flushed into the groundwater system and the system becomes increasingly saline. In contrast to this, during the drier periods when groundwater is extensively used and the only source of water, the salinity does not increase but the groundwater source is at risk of being depleted. In Namaqualand it's the very events that made the region so usable during periods of higher rainfall (Dewar & Stewart, 2017) that resulted in difficulties such as saline groundwater, in the drier periods when the groundwater resources are most used.

4.6. Conclusions

The ages of the carbonates in the heuweltjies provide valuable information regarding the climate in the past which can in turn be related to periods of recharge during which salts being flushed into the groundwater system. Furthermore, the distribution of the carbonate ages indicate that the water preferentially flows through the center of the heuweltjie compared to the edges. This would imply that heuweltjies preferentially facilitate recharge. Although the origin of the salt present in the heuweltjies are a combination of dry deposition of marine and non-sea salts, these salts have accumulated in heuweltjies over thousands of years. Heuweltjies therefore contribute to the salinity of the groundwater as heuweltjies act as salt storage zones and the salts in the heuweltjies can be related to the salts in the groundwater through the $\delta^{18}O\ SO_4^{2-}$ and $\delta^{34}S\ SO_4^{2-}$ isotope signatures. $\delta^{18}O\ SO_4^{2-}$ and $\delta^{34}S\ SO_4^{2-}$ together with $^{87}Sr/^{86}Sr$ isotope signatures also showed that water-rock interaction plays a role in controlling the groundwater chemistry, specifically in the case of the fractured granitic gneiss aquifer host rocks. For the last 18 000 years Cl^- has been flushed into the groundwater system in various concentrations but three periods of recharge are worth noting where less soluble salts such as gypsum and even carbonates were flushed into the groundwater system. These are around 14 000 ybp, around 8000 ybp, in the Mid-Holocene Altithermal around 5600 years ago, in the early Neogene Period around 2000 years ago and the last significant event was at the beginning of the Little Ice Age around 600 years ago. The climate change predictions of increased frequency and more intense rainfall events may have an effect on the proportion modern recharge but salts will also be flushed into the system during these events, further increasing the salinity of the groundwater in the catchment. Apart from the climatic implications highlighted in this study, it was shown that the previous understanding that termite nests are water sheds is not always true as heuweltjies, facilitate the downward movement of water within soils and that water movement in termite affected soils in should be further investigated.

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CHAPTER 5.

Conclusions and Recommendations

5.1. Conclusions

Natural salinisation of soils and groundwater occurs across various climatic regions, but in semi-arid to arid environments this phenomenon is generally ascribed to the high evaporation rates coupled with low mean annual rainfall. However, this is not always the case. Given that the population in sub-Saharan Africa is expected to increase by 45% in the next 20-30 years and that surface water resources in this region won't be able to sustain the population, many communities will rely on groundwater as their only source of potable water, if they aren't already doing so (Gerten *et al.*, 2011; Ojeda Olivares *et al.*, 2020; UNDESA - United Nations, Department of Economic and Social Affairs, 2017). With much of sub-Saharan Africa experiencing semi-arid to arid climatic conditions and being one of the region's most vulnerable to climate change, it is important to understand the factors that play a role in the sustainability of the groundwater resources, both in terms of quality and quantity. In this study, it was shown that biophysical features, heuweltjies, play a large role in groundwater salinisation in a semi-arid to arid environment and have been doing so for thousands of years. Although there is some controversy exists regarding the formation of heuweltjies, but most authors agree that heuweltjies are the result of termite activity, more specifically *Microhodotermes viator* (McAuliffe, Hoffman, McFadden, Jack, *et al.*, 2019; Moore & Picker, 1991b; Picker *et al.*, 2007; Potts *et al.*, 2009). Given that termites, though not the same species, occur all over Africa and in many other parts of the world, it is likely that other groundwater sources may also be affected by termite related salinisation.

5.1.1. *Groundwater in the Buffels River catchment*

The Buffels River catchment experiences semi-arid to arid climatic conditions and many communities are wholly reliant on groundwater as their only source of potable water. In addition to this, much of the local economy is also reliant on groundwater but the groundwater is variably saline which poses a risk to both human health and the economy. In order to better constrain the extent and cause of salinisation in the region a combination of various isotopes and basic hydrochemistry was used. Saline groundwater in the Buffels River catchment is hosted in in both alluvial and fractured rock aquifers. Low ^{87}Sr/^{86}Sr ratios together with patterns and trends in the groundwater chemistry suggest that several isolated alluvial aquifer systems exist. One large known alluvial aquifer, the Spektakel Aquifer situated in the Buffels River valley, is the least saline of the alluvial aquifers, while the smaller more isolated alluvial aquifers to the east and the west of the Spektakel aquifer host more saline groundwater. The chemistry of groundwater hosted in fractured aquifer systems were related to the specific host rock by using the variation in ^{87}Sr/^{86}Sr ratios in combination with major cations and anions.

Elevated $^{87}Sr/^{86}Sr$ ratios confirmed that the host rocks are different granitic gneisses as these rocks are highly radiogenic in this region.

In terms of the groundwater chemistry, most of the major cation and anion concentrations in the groundwater from the Buffels River catchment are elevated, but the main concerns are elevated Na^+, Cl^- and SO_4^{2-} concentrations. These concentrations are in most cases above the limits of the World Health Organisation standards for drinking water, but yet the water is still utilised as potable water. Local water management authorities should be advised on this and assisted in finding a solution to treat the water to drinking water standards. Given the elevated Na and Cl concentrations, it was previously thought that evaporative concentration of salts followed by flushing events is the leading cause of salinisation in this region. However, $\delta^{18}O$ and δ^2H isotope plots showed no distinct evaporation trend and it was established that this process could play a minor role in salinisation but does not appear to be the leading cause of salinisation in the Buffels River catchment. Instead, the dry deposition of marine aerosols containing salts and water-rock interaction also plays a role in controlling the groundwater chemistry. Once in the aquifer, ion exchange and mineral weathering reactions may alter the groundwater chemistry. Although, salts are not produced in heuweltjies, they act as salt storage zones. Geophysics data indicated that ECa values (a proxy for salinity) are the highest in the centre of heuweltjies and that these values increase with depth in heuweltjies. This was one of the first indications that heuweltjies could potentially contribute to groundwater salinisation.

5.1.2. *Groundwater sustainability in the Buffels River catchment*

Groundwater sustainability in this region, in terms of quantity and quality is questionable. Although salinisation processes are directly related to the quality of groundwater, groundwater ages and temporal relationships are also related to the sustainability of the resource. The use of conventional radiocarbon age calculations with a dilution factor was evaluated and in doing so, the variability of $\delta^{13}C_{DIC}$ values was assessed together with the effect that factors such as geology and vegetation (C3 and C4 species) may have on $\delta^{13}C_{DIC}$ values. The heterogeneity in $\delta^{13}C_{DIC}$ values resulted in testing of multiple scenarios with different dilution factors but none of these preliminary scenarios provided sensible ages from the calculations. The challenges encountered using conventional radiocarbon calculations in a semi-arid to arid silicate dominated environment, showed that alternative models should be used, especially if there is very little pre-existing data for the area. A new groundwater recharge model was conceptualised to include factors that may have an impact on the groundwater chemistry and hence the radiocarbon ages. Heuweltjies or the variability of the aquifer type or host rock have not been included in the previous understanding of groundwater flow and recharge paths and the new conceptual model for groundwater recharge in the Buffels River catchment was constructed to include all these variables. The simplified conceptual model for groundwater hosted in the Buffels River catchment suggests that recharge occurs in three potential ways. 1) direct recharge into the fractured system through the fracture network; 2) in areas where thin soil horizons exist, groundwater will move through the soil horizon and into saturated zone, from where it may flow into the fractured system if the fracture network allows it; 3) where thicker soils exist, heuweltjies may be present. Here, the water will preferentially flow through the tunnels and bioturbated soils where it will either end up in the saturated zone or flow onto the granitic basement. If water enters the saturated zone, small localised aquifers could form above the granitic basement from where the water will move into the granitic basement system through fracture networks where they exist.

Given that the geology of the catchment is dominated by granitic gneisses and the only inorganic carbon present in the system is found in heuweltjies, together with the fact that heuweltjies behave as open-systems when groundwater passes through them, the radiocarbon signature in groundwater is likely to be dominated by decay rather than dilution. However, the presence of tritium together with low radiocarbon activities suggested that modern recharge to older groundwaters may be occurring and a simplified and theoretical lumped parameter model approach was used to calculate total mean ages. For the most part, groundwater in the Buffels River catchment can be classified as young groundwater (recharge received between 12 000 and 50 years ago). Groundwater towards the east of the catchment has a fossil component, while only samples from five locations can be classified as modern groundwater with ages younger than 50 years. These five samples were all situated towards the middle of the catchment. Although the average percentage modern recharge in the catchment is 24.75%, the recharge is not spatially uniform and has implications for the local communities in terms of the future groundwater availability and quality. In areas where groundwater resources are already under pressure, some measures will have to be put in place to manage the use of groundwater as many of the boreholes have dried up or are starting to do so. The fact that modern recharge in some areas are as little as 8.0%, alternative resources should be investigated as there is a risk of exploiting older or fossil groundwater resources that are not regularly recharged, which is likely to leave the region without a reliable water resource. Although the conceptual model is simplified, it should be used as a base to start educating the local authorities about the groundwater system and the risks involved in tapping into the fossil groundwater. These resources may not be renewable and will not necessarily be able to sustain the local water requirements in the long term.

5.1.3. *Heuweltjies and salinisation*

Salinisation has not been a continuous process in the Buffels River catchment but it has rather occurred as specific events over time. Specific increases in the EC and anion concentrations of groundwater have been recognised. In order to validate the salinisation events, the ages and distribution of carbonates in heuweltjies were determined and used as a proxy for salinisation periods. Radiocarbon age dating on heuweltjie carbonates revealed that heuweltjie soils date back to between ~35 400 years and ~2 700 years before present. Along the edges of the heuweltjies, soil ages increase with depth while a similar pattern was observed in the centre of the heuweltjies, but soils with the same ages as that found along the edges, are situated much deeper. The depth to the carbonate horizons in calcareous heuweltjie soils was used as a proxy to assess the flow paths of water through the heuweltjie and a clear U-shaped wetting front is recognised. This suggests that heuweltjies facilitate downward movement of groundwater with termite nests facilitating the water movement. The ages of these wetting events are comparable to the groundwater ages and to periods of major increases in dissolved salts in the groundwater over the past 18 000 years. This suggests that although the groundwater ages were calculated as theoretical ages, they can be correlated to the ages of the wetting fronts and hence recharge periods. During wetter and more humid periods in the past 18 000 years (Neogene period and the Little Ice Age), recharge occurred during which salts were flushed into the groundwater system.

The salts stored in heuweltjies were related to saline groundwater by using $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$. In areas of higher heuweltjies densities, the $\delta^{34}S\ SO_4^{2-}$ and $\delta^{18}O\ SO_4^{2-}$ isotope signatures of heuweltjies soils and groundwater are comparable. This suggests that groundwater is vulnerable to salinisation caused by heuweltjie and hence termite affected soils. Saline groundwater in regions of lower heuweltjie density was related to the influence of water-rock interaction together with salinisation because of dry deposition of marine aerosols. Although the salinisation process in the Buffels River catchment is a natural process that cannot be prevented, the previous idea of salinisation occurring because of the evaporative concentration in the arid climate has now been proved incorrect. Salinisation in the Buffels River catchment is a more complex process where aerosols containing marine and non-marine-salts are either stored in the heuweltjies before being flushed into the alluvial aquifers or directly transported into the fractured aquifers where the heuweltjie density is low. Once in the fractured aquifer, water-rock interaction controls the chemistry. The flushing events mostly occurred in the wet and humid periods in the past 18 000 years proving that salinisation of groundwater in the Buffels River catchment is related to periods of increased rainfall and humidity. Future climate predictions for Namaqualand and the west coast of southern Africa include periods of prolonged drought, but erratic and intense rainfall events are also expected. During the periods of drought, groundwater will be necessary to sustain the social and economic needs of the region but when intense rainfall events occur there is a risk salts stored in heuweltjies being flushed into the system, resulting in increasingly saline groundwater. Given that groundwater sustains much of the communities' needs as well as a large part of the economic sector, plans should be made to find alternative water resources or treating the groundwater that is available to meet the requirements of what it will be used for.

This study has shown that heuweltjies can be used as a proxy for saline groundwater. If it is assumed that heuweltjies are related to termite activity as many authors have confirmed, the mounds of other species of termites in other parts of the world can also possibly be used as a proxy for saline soils and groundwater. In the Buffels river catchment, groundwater hosted in the fractured aquifer is relatively unaffected by the heuweltjie salts which can be related to the extremely thin if any soils above the bedrock and hence low heuweltjie density. However, the alluvial aquifers or aquifers present where thick sediments exist are affected by the heuweltjie salts. Many communities in sub-Saharan Africa are becoming increasingly dependent on groundwater, mainly tapped from alluvial aquifers which are more easily accessible that deeper fractured systems, biophysical features such as termite mounds could be used as indicators of groundwater quality.

Although it is uncertain whether the mounds of all termites are associated with salt accumulation, termite activity facilitate downward movement of groundwater through the tunnels and bioturbated soils. This has implications for contamination of groundwater sources. Heuweltjies are present in large parts of the Western Cape of South Africa (Cramer *et al.*, 2017; Midgley, Harris, Harington, *et al.*, 2012b; Picker *et al.*, 2007), which is also one of the large crop producing agricultural regions in southern Africa and also heavily dependent on groundwater. A small fraction of the fresh produce from this region is for local use while the rest is for international markets. Apart from groundwater and soil salinisation, heuweltjies facilitate rapid groundwater recharge and given that intensive agriculture requires fertilization and the application of pesticides and herbicides, heuweltjies increase the risk of contaminating the groundwater resources. Moreover, there is a risk that this contaminated water is reused as groundwater in this region is often used for irrigation purposes.

5.2. Recommendations

This study has shown that there is a relationship between saline groundwater and heuweltjies in the Buffels River catchment in the Northern Cape of South Africa. It was also found that salinisation of groundwater in this region is not a continuous process but occurs during wetter and more humid periods during which the dependence on groundwater will decrease as enough surface water will be available. A few recommendations can be made with regards to the managing the impact of heuweltjies and saline groundwater and future research that should be conducted:

- The conceptual model should be refined and incorporated into a large-scale hydrological model for the Buffels River catchment to better the understanding regarding of the large-scale impact that heuweltjies may have on groundwater chemistry and recharge.
- To establish an aquifer specfic groundwater management plan. The alluvial aquifer systems and the fractured rock aquifer systems should be better delineated and the management of these aquifers should relate to their different properties.
- To educate authorities, local communities, and farmers in regions where heuweltjies occur in high densities (including other parts of South Africa) about the relationship between heuweltjies, saline soils and saline groundwater for the purposes of future developments and investments.
- To further understand the dynamics salt accumulation in heuweltjies and to compare that to termite mounds in other regions.
- To evaluate the relationship between termite activity and saline soils and groundwater in other parts of the world.
- To assess if preferential flow paths caused by termite activity contribute to increased concentrations of agricultural contaminants (pesticides, fertiliser and herbicides) in groundwater in areas where agriculture is the dominant land. This is specifically applicatble along the south-west coast of Southern Africa.
- To investigate the relationship between past climatic periods, heuweltjie ages and groundwater salinisation periods in other regions with similar climatic conditions to refine the understanding of the impact that climate change had and may have on groundwater quality.
- To use heuweltjie carbonate isotope data for paleoclimate reconstruction to aid in the future climate predictions.

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