Characterizing water quality of rivers and underlying aquifers in the Nuwejaars Catchment, South Africa

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In

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DECLARATION

I, Errol Masuzyo Malijani declare that *Characterizing water quality of rivers and underlying aquifers in the Nuwejaars Catchment, South Africa* is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

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ABSTRACT

Non-perennial rivers are the main source of surface water in drylands. These rivers are unpredictable and highly variable in terms of flow regime and water quality. Despite their abundance, and importance in the landscape, non-perennial rivers still remain under- studied. The functioning of non-perennial rivers seems to be strongly dependent on groundwater, especially during dry seasons when pools develop, but the relationship between surface water and groundwater has seldom been established and quantified. Many of these systems are ungauged and hydrological and chemical data are available for very few systems in South Africa.

The present study falls under the Non-perennial Rivers Project, and aimed to characterize the water quality of rivers and aquifers in the Nuwejaars Catchment, located in Cape Agulhas, near the southern-most tip of Africa. To achieve this aim, a quantitative approach that provides the ability to assess relationships between variables both spatially and temporally was applied. Field visits were conducted on four occasions during July 2017 and July 2018, to characterize the chemistry of surface water and groundwater during dry and wet seasons. Physical parameters were measured *in situ*, while water samples were collected from boreholes, piezometers, springs, artesian boreholes and selected points along the river for laboratory analysis of major ions, nutrients and stable isotopes. Descriptive and bivariate statistical methods were used to summarise and evaluate the strength of the relationship between variables, while multivariate statistical methods were applied to group similar samples based on their chemical compositions. Piper diagrams were generated to characterize water type based on the proportions of cations and anions, while correlation and stoichiometric analysis was applied to identify hydrogeochemical processes influencing groundwater chemistry. Stable isotope compositions were presented on a graph, along with the global meteoric water line (GMWL) and local meteoric water line (LMWL) to establish similarities between isotope signatures of groundwater and surface water.

Results indicate that groundwater, especially shallow groundwater in the lower parts of the catchment is saline. Electric conductivity (EC) in surface water was variable, ranging between 45.2 and 3740 mS/m, with waters within the Table Mountain Group region (TMG), recording the lowest values. Artesian boreholes were fresh with an average EC usually below 50 mS/m, while higher EC values of a minimum and maximum value of 2379 and 6620 mS/m were recorded from shallow groundwater during the sampling period. Generally, EC values increased from the upper TMG region of the catchment towards the Bokkerveld shale region downstream and were highest during the dry season of 2018, with the exception of surface water that recorded the highest mean value during the wet season of 2017. The results indicate strong geological influences on water chemistry.

Groundwater and surface water pH values generally ranged between 5 and 8, however pH values below 5 were recorded in groundwater upstream. An increasing trend in pH from the uplands to the lower sections of the catchment was observed in both groundwater and surface water. Major ion compositions were present in the following order of abundance; Cl^- > Na^+ > Mg^{2+} > SO^{2-}_4 > Ca^{2+} > HCO^-_3 > K^+, throughout the sampling period in all waters of the Nuwejaars Catchment. Sodium and chloride were the dominant major ions, therefore the water type was characterized as sodium-chloride water. Nutrient concentrations were low, measuring values usually below 1 mg/L for nitrate and total nitrogen, while phosphate and total phosphorus typically measured values below 3 mg/L, however occasional increased concentrations were observed. These concentrations do not suggest that agricultural practices largely influence water quality within the catchment. Evaporation, ion exchange, reverse ion exchange, carbonate and silicate weathering were identified as hydrogeochemical processes influencing groundwater chemistry.

Isotope compositions in groundwater showed slight variations during the summer and winter seasons of 2018, ranging between -24 to -5.9 ‰ for δ^2H and -5.5 to -1.7 ‰ for $\delta^{18}O$ during summer, while in winter, compositions ranged between -24.5 to -8.9 ‰ for δ^2H and -4.8 to -2.2 ‰ for $\delta^{18}O$. In surface water, seasonal variations in isotope compositions were more pronounced ranging between -22.9 to 38.8 ‰ for δ^2H and -5.1 to 7.1 ‰ for $\delta^{18}O$, during the summer season. In winter, isotope compositions in surface water were less enriched, ranging between -21.1 to 9 ‰ for δ^2H and -4.9 to 0.9 ‰ for $\delta^{18}O$. Groundwater samples clustered between the LMWL and GMWL and were characterized by similar isotopic compositions to that of local rainfall. This indicates that direct infiltration is the source of groundwater in the study area. Results from the isotope analysis also established a connection between surface water and groundwater in the upper regions of the catchment. Isotope signatures of surface water upstream were similar to those of groundwater in the uplands, showing evidence of the connectivity between groundwater and surface water in this region. The results obtained from this study provide a comprehensive understanding of water quality and factors that influence the chemistry of water resources in the Nuwejaars Catchment. This information will inform the basis for better decision making and the management of N-PRs, as well as provide chemical data for studies to follow under the Non-perennial Rivers project.

DEDICATION

This thesis is dedicated to my family. To my mom Dawn Negonde, thank you for all the sacrifices you made to ensure my success. Your unconditional love and encouragement have kept me going.

To my siblings, nieces and other family members, I appreciate the constant love and support. Thank you for always believing in me.

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Table of Contents

List of Figures

List of Tables

Abbreviations and Acronyms

° C	degree Celsius
‰	Parts per mill
Ca^{2+}	Calcium ion
Cl^-	Chloride ion
DO	Dissolved oxygen
EC	Electric conductivity
HCO^-_3	Bicarbonate ion
K^+	Potassium ion
meq/L	Milli equivalents per Litre
mg/L	Milligrams per Litre
Mg^{2+}	Magnesium ion
mS/m	MilliSiemens per meter
Na^+	Sodium ion
N-PRs	Non perennial rivers
SO^{2-}_4	Sulphate ion
TMG	Table Mountain Group
TN	Total nitrogen
TP	Total phosphorus
TWQR	Target water quality range
$\delta^{18}O$	Oxygen- 18
$\delta^{2}H$	Deuterium

Chapter 1: Introduction

1.1 Introduction

South Africa is a semi-arid country characterized by high temperatures, a mean annual rainfall of 450 mm/a, and high evaporation rates that are four times greater than the total annual precipitation (Dent et al., 1987; Diamond, 2014). The Western Cape Province, in particular, receives approximately 348 mm/a of rainfall and experiences vast differences in average annual rainfall across the province (Diamond, 2014). As a result, non-perennial rivers (N-PRs) are dominant in semi-arid to arid regions, which make up approximately two thirds of South Africa (Digout, 2002; Seaman et al., 2013). Furthermore, due to drying patterns and other effects of climate change, the number and proportions of N-PRs are expected to increase (Larned et al., 2010). N-PRs differ from perennial rivers in terms of their flow regimes, periods of cessation of flow, as well as their overall water chemistry characteristics (Seaman et al., 2016). The cessation of flow and drying in these systems is driven by processes such as evapo-transpiration, seepage and lowered groundwater tables (Larned et al., 2010). These systems are thus characterized by unpredictable fluctuations in flow, large sediment loads, and poorly structured faunal assemblages that are constantly under immense pressure (Larned et al., 2010; Seaman et al., 2013).

Groundwater plays an important role in the functioning of N-PRs, especially during the dry season. A connection between groundwater and surface water allows for pools to develop as a result of groundwater discharging to the surface. Groundwater is therefore likely to influence the water quality of pools, as well as their persistence especially during the dry season (Seaman et al., 2013). In the absence of perennial rivers, N-PRs serve as the primary sources of fresh water in most arid regions (Rossouw et al., 2005). In addition, N-PRs also play a major role in supporting and maintaining vegetation and other biotic communities, as well as functioning as flood control systems during high flows (Tal et al., 2010).

The Non-perennial Rivers Project, the larger project that the current study falls under, is based on a multi-disciplinary approach that involves the collaboration of individuals from different disciplines (hydrology, geohydrology, water quality and geomorphology). This approach, allows for forward and backward exchanges of information between disciplines and the ability to widely investigate different aspects of N-PRs. Objectives set out for the water quality component in particular, included, assessing the temporal and spatial variations of water quality in water resources, as well as, identifying factors or processes that influence these variations. This study focused on the water quality component of surface water and groundwater in N- PRs, using the Nuwejaars Catchment, a costal catchment within the Overberg East region of the Western Cape Province of South Africa as a case study. Over a cycle of seasons, concentrations of chemical constituents and magnitudes of physical attributes in the form of in-situ parameters, nutrients, major ions and environmental isotopes were assessed. Previous studies by Herdien et al. (2005) and Mazvimavi (2017), recommended the initiation of research that would assist in understanding the spatial and temporal variations of water quality within the Nuwejaars Catchment. Mazvimavi (2017) reports on preliminary findings with regards to several aspects of water resources within the study area, obtained from studies conducted by the University of the Western Cape.

Literature surrounding N-PRs recognizes the complexity of these systems and the challenges experienced when general practices developed for perennial rivers are applied to these systems. Seaman et al. (2010) emphasised that, hydrological models, water quality records and assessment methods, obtained for perennial rivers over the years, are not always applicable to non-perennial systems because the two types of rivers are so different from each other hydrologically and chemically. Furthermore, due to their considerable dependence on groundwater, the quality of N-PRs can be drastically affected by the water quality of the aquifers that fed them, another aspect that adds to the complexity of these systems. Rossouw et al. (2005) reported that, because the relationship between flow and water quality in N-PRs is not well understood the ecological effects and water chemistry changes that result from the drastic flow fluctuations experienced in N-PRs are not well understood.

Despite their importance, N-PRs still remain under-studied and neglected by both policy makers and scientists, ultimately resulting in a lack of understanding on how these systems function (Seely et al., 2003; Larned et al., 2010). This is a general problem highlighted in both local and global literature across different spheres of water resource studies and has been attributed to the complexity and nature of these systems. In particular, water quality parameters of most surface waters in the Western Cape region of South Africa, which are predominantly non-perennial, are often difficult to measure and historical data is minimal (Herdien et al., 2005). Consequently, the extrapolation of chemical data from previous studies that provides a comprehensive understanding of water quality in N-PRs is often a challenge. Natural or reference water quality conditions in these systems are therefore usually unknown. According to Seamen et al. (2010), setting a reference condition for water quality in these systems is difficult and usually an “educated guess” and cannot be based on any real scientific evidence. However, more specific to the current study, according to Mazvimavi (2017) water resources within the Nuwejaars Catchment are not sufficiently monitored by the Department of Water and Sanitation, limiting available water quality records. Similarly to other dryland regions, detailed information that pertains to the chemistry of water resources within the catchment is generally lacking. Consequently, water quality of rivers and aquifers within the catchment is not well characterized. Furthermore, concerns regarding the effects of agricultural practices near the floodplain of the Nuwejaars River on water chemistry have also been reported on. This warrants research that will address these specific problems within the catchment.

Concerns regarding the poor management of non-perennial rivers have been expressed in previous studies (Tal et al., 2010; Skoulikidis et al., 2017). Unless the quality of rivers and aquifers in N-PRs is characterized, assessed, monitored and documented, the proper management of water resources within these systems cannot be achieved. This limits the ability to assess impacts of human activities, and identify changes in water quality over time. These changes have the potential to significantly affect the ecosystems that depend on the fresh water provided by N-PRs, especially in dry regions. In addition, knowledge regarding the chemistry of rivers will remain focused on perennial rivers and progress towards improving and modifying management and assessment methods that consider N-PRs will not be achieved. Challenges regarding the allocation of water, particularly suitable for irrigation in semi-arid regions are likely to worsen over time if the chemistry of N-PRs remains unknown. In the study area, due to limited fresh water and increasing water demands, water allocation challenges currently exist and the need for an alternative water resource intensifies. This is a challenge that, the Breede-Gouritz Catchment Management Agency (BGCMA), responsible for water allocation within the region can only resolve when adequate information on water quality within the catchment has been obtained.

1.2 Research questions

To address the research problem outlined, the main research question of the current study is, what is the nature of surface and groundwater quality in non-perennial river systems, within semi-arid regions?

Four sub-questions that were chosen to answer the main question include:

1.1.1 How do chemical compositions of groundwater and surface water in non-perennial river systems vary spatially and temporally?

1.1.2 What are the hydrogeochemical processes influencing groundwater chemistry?

1.1.3 Is groundwater and surface water in the Nuwejaars Catchment connected?

1.3 Study aim and objectives

The aim of this study was to characterize the water chemistry of rivers and associated aquifers in the Nuwejaars Catchment. This would provide information on the quality of water and factors that influence the chemistry of water resources in non-perennial river systems, which would also inform the basis for better decision making and the management of N-PRs.

To achieve the aim, the objectives of the study were to:

- Assess a number of physico-chemical variables of groundwater and surface water to establish temporal and spatial variations in water quality.
- Identify hydrogeochemical processes that influence groundwater chemistry.
- Assess isotope signatures to establish interactions between groundwater and surface water.

1.4 Thesis outline

Chapter 1 (Introduction): provides a brief background and general introduction to the topic, which outlines the main concepts, rationale and scope of the study. The research problem, research questions, aims and objectives to be addressed by the current study are also outlined.

Chapter 2 (Literature review): provides a review of literature concerning, non-perennial rivers and water quality related issues in semi-arid regions. This chapter also discusses major constitutes of water and approaches commonly used for the characterization of water quality. The theoretical framework which provides the principles and theories guiding the current study are also included.

Chapter 3 (Study area): provides insight on the general setting and location of the study area and a description of the specific experimental study sites. This chapter particularly focuses on describing the climate, topography, geology and land-use activities of the study area.

Chapter 4 (Research design and methods): outlines the methods and procedures used to collect, prepare, analyse and interpret water chemistry data. Information is also provided on the various software packages used in the analyses.

Chapter 5 (Results and discussion): describes the results of the chemical analyses, particularly highlighting spatial and temporal variations in water chemistry. This chapter also attempts to identify hydrogeochemical processes influencing groundwater quality and interactions between groundwater and surface water.

Chapter 6 (Conclusions and recommendations): provides a brief summary of the main findings for each objective. This chapter also provides recommendations for water resource managers and for future research and monitoring.

Chapter 2: Literature Review

2.1 Introduction

This chapter critically reviews global and local literature with respect to the water quality of non-perennial rivers and aquifers, particularly in arid regions. The definition and characteristics of N-PRs are discussed, as well as the contribution of groundwater to these systems. Key constitutes of water quality and methods for hydrogeochemical characterization are reviewed, followed by an in-depth review on environmental isotopes as tracers in water chemistry. Lastly, the theoretical framework which provides a synthesis of theories and principles that govern processes influencing the chemical composition of rivers and aquifers is provided.

2.2 Definition of Non-perennial Rivers

The term non-perennial with regard to rivers is collectively used to describe or refer to, temporary, intermittent, ephemeral and episodic rivers. Rossouw et al. (2005) defined N-PRs as semi-permanent rivers experiencing no flow for 1-25% of the time, ephemeral rivers with no flow 26-75 % of the time, and episodic rivers that flow only after a high rainfall event, with no flow at least 76% of the time. The definition provided by Rossouw et al. (2005), is similar to that provided by Seaman et al. (2010), which divided the hydrological continuum of rivers into 4 categories. The four broad categories and hydrological continuum as described by Seaman et al. (2010) that describes the flow regime of South African rivers are presented in Figure 1. Seaman et al. (2010) emphasized that, although the boundaries specified for each category were useful in assisting with decision making, the dashed lines indicate that these boundaries are not fixed and only serve as an indication.

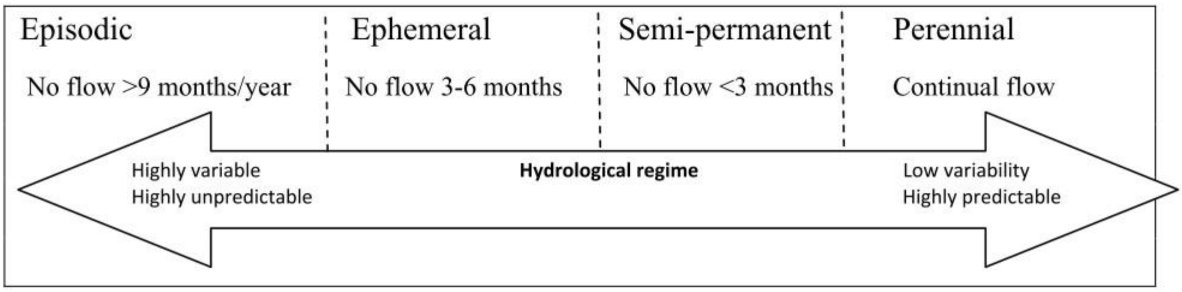


Figure 1: A conceptual framework of the four categories and the hydrological continuum of South African rivers, adapted from Seaman et al. (2010).

Previously, Uys and O'Keeffe (1997) had also attempted to classify and define N-PRs according to their hydrological features. Various factors such as flow duration, periods of flow and no flow, the time of the year at which flow commenced, and the variable and unpredictable flow regime of N-PRs, were considered. These authors defined N-PRs as temporary rivers that experience the cessation of flow within the channel yearly or within 2 or more years in a period of

5 years; intermittent rivers as those that cease to flow in certain sections of the channel for a variable period of time and may flow seasonally; ephemeral rivers as those that flow briefly, usually for a period less than the period in which they are dry, and lastly, episodic rivers as those that flow after a flood or high-rainfall event. For the purpose of the current study the term N-PRs refers to temporary, intermittent, episodic and ephemeral rivers, as classified by Uys and O’Keeffe (1997). Rossouw et al. (2005) emphasised the need to clearly define N-PRs, and to separate them from perennial rivers, since differences in their functionality had been established.

2.3 The abundance and importance of Non-perennial Rivers

The effects of aridity in Africa are intense and widespread, and nearly half of the rivers in South Africa are non-perennial (Rossouw et al., 2005). According to Datry et al. (2014), N-PRs are a common feature globally, and have been estimated to make up at least 50% of global river systems (Skoulikidis et al., 2017). According to Mosley (2015), the number of N-PRs is expected to increase globally, as more and more permanent rivers become seasonal as a result of increased river abstractions, droughts, unpredictable rainfall patterns and high evaporation rates. Although found worldwide, N-PRs are mostly concentrated in Mediterranean regions, regions that are known for their ecological value, with unique faunas and floras. In France, at least 20-39% of river networks are non-perennial, while in Italy as many as 90% of all river systems are no longer permanent. Only 45 out of the recorded 765 rivers and streams in Greece flow permanently (Skoulikidis et al., 2017). Even so, N-PRs still remain under-studied, regardless of their abundance and ecological importance (Tal et al., 2010). Tal et al. (2010) and Skoulikidis et al. (2017) expressed their concern regarding the poor management of non- perennial systems, especially because of the role they play in maintaining biodiversity and flood control. N-PRs play an important role in supporting ecosystems, by providing much needed water for the vegetation and fauna that grow in arid regions. In areas where freshwater is limited, N-PRs are important for the survival of humans and other animals.

2.4 The Role of groundwater in N-PRs

Groundwater plays an important role in the functioning of N-PRs by contributing to base flow (Parsons, 2004; Rossouw et al., 2005. This contribution can alter the water quality of surface water, to a quality that is similar to that of groundwater discharging to the surface. Dryland rivers may also recharge aquifers (Rau et al., 2017). During dry seasons, where a connection between groundwater and surface water exists, pools may develop as a result of groundwater discharging to the surface (Seaman et al., 2013). The pools that form are of great ecological importance, especially for the surrounding biota during dry periods (Hughes, 2008; Seaman et al., 2013). The extent of this contribution is dependent on factors such as the hydraulic head and the resistance of media between the two systems (Rossouw et al., 2005; Seaman et al., 2016. According to Rau et al. (2017), shallow groundwater is in fact the main source of fresh water in these systems during dry seasons. Several studies have previously emphasised the importance of groundwater in N-PRs (Rossouw et al., 2005; Seaman et al., 2010).

The formation and persistence of pools is highly dependent on the movement of water between surface and groundwater, especially surface-sub-surface flow. This link is poorly understood (Rau et al., 2017), regardless of the fact that the number of studies within regards to interactions between groundwater and surface water have increased exponentially over the last decade (Larned et al., 2015). Rossouw et al. (2005) and Seaman et al. (2013) have stated that surface-groundwater interactions in such unpredictable systems are complex and not easy to understand. Understanding the link between groundwater and surface water in N-PRs is a crucial component when assessing the movement of water in these complex systems (Rau et al., 2017).

2.5 Variations of water quality in South African Rivers

Water quality challenges are experienced in one form or the other globally. For instance Sprague et al. (2009), reported on the degradation of river systems in the USA, identifying phosphorus and nitrogen as leading pollutants in river systems. On the other hand Kumar et al. (2017) reported on the deterioration of water quality in India primarily due to population growth, growing industries, and the use of fertilizers. Although the circumstances may differ, most regions in the world are experiencing some type of challenge in terms of water resource protection and management.

Water quality differs across continents, from region to region and even at a catchment scale mainly due to differences in climate, geology and vegetation, as well as geomorphological features (Day et al., 1998; Dallas and Day, 2004). The climate of South Africa in particular is very diverse, resulting in a rainfall gradient from east to west and south to north. The south and east regions are characterized by a moderate climate with a considerable amount of rainfall as compared to the rest of the country. As a result, most of the river systems in the south and east are perennial and the water is generally of good quality. They mostly exhibit low salinity levels, because of constant flow and a limited amount of evaporation. However, in the arid regions to the north and west, the opposite is evident: most rivers are non-perennial, and periodically experience little to no flow. These systems are highly saline due to high evaporation rates.

Differences in lithology also influence the water quality of rivers, and since South Africa is geologically diverse, variations is water chemistry exist across the country. The Karoo Basin, the Transvaal and Drakensberg regions of South Africa, are characterized by igneous formations that contain significant quantities of calcium and magnesium ions and are further defined by low conductivities and a pH above 7. Rivers within these regions also contain significant amounts of phosphates, nitrates and silicates (Day and King, 1995). According to Gibbs (1970) these rivers are primarily influenced by geological features and are therefore “rock dominated waters”. On the contrary, the south-western parts of the country underlain by the Table Mountain Sandstones of the Cape Supergroup are dominated by sodium and chloride ions, although this pattern changes with distance inland (Day and King, 1995). Due to the weathered nature of the Table Mountain Group formations, these rivers are generally of good quality, with low nutrient, ion and conductivity concentrations, if not influenced by human activities (Dallas and Day, 2004). These rivers also generally tend to be acidic in nature and were referred to as “precipitation dominated water” by Gibbs (1970).

2.6 Major water quality constituents

2.6.1 Temperature

The temperature of flowing water is dependent on hydrological factors, such as the source of the water (snow, rainfall, surface runoff, and groundwater discharge) and the climatic characteristics of the region (Dallas and Day, 2004). The structural features of a river channel such as channel morphology (channel form, depth and structure), topography and surrounding land cover also have an influence on the temperature of flowing rivers. According to Lambing (1983), deeper streams show less variations in temperature than shallow streams do, and therefore depth is a strong influence on water temperature in rivers. Global temperature models have predicted significant temperature changes as a result of climate change; such meteorological changes will significantly alter the thermal regimes of surface waters and shallow aquifers (Kurylyk et al., 2013).

Temperature is less variable in groundwater than it is in rivers, as it is not in direct contact with the air. Water temperature can be used as an indication of groundwater – surface water interactions. The thermal regime of groundwater is influenced by changes in water and energy fluxes. Water temperatures fluctuate seasonally and even daily depending on many different factors, some even anthropogenic. In summer, when surface water temperatures are high, groundwater discharges regulates temperatures in rivers (Kurylyk et al., 2013). In general, the natural water temperature of groundwater is representative of the temperature of incoming recharge from the surface. The shallow zone of an aquifer may be affected by seasonal changes in temperature. Shallow permeable aquifers during summer tend to have higher water temperatures as compared to deep groundwater within the saturated zone; the opposite occurs during winter. Groundwater that is approximately 5-150 m below the surface tends to be closely related to mean annual air temperatures. Temperature generally increases gradually with depth in areas where the aquifer receives direct recharge from the surface (Younger, 2007). The TWQR for water temperature is case and site specific and can be based on local conditions within an area.

Various physical, chemical and biological processes are dependent on, and are directly affected by, water temperature. Aquatic species have a temperature tolerance range in which they can survive and thrive, and drastic changes in water temperature may be fatal for some species (Dallas and Day, 2004). For example, some species of warm-water fishes require a very narrow temperature range of 23.9°C to 26.7 °C for successful spawning and egg development (Lambing ,1983). Most aquatic species are cold-blooded (poikilothermic), being unable to regulate their temperatures and therefore having the same temperature as the water in which they live (Dallas and Day, 2004). Higher water temperatures reduce the solubility of dissolved oxygen, resulting in a decrease in its concentration and limiting its availability to aquatic organisms. The severity of effects on aquatic organisms caused by water temperature changes depends on the extent, duration and timing at which these changes occur. Small gradual changes, if maintained for an extended period of time, may result in severe effects on organisms while rapid and large temperature changes may be fatal. Water temperature prompts the timing of migration and spawning. Artificial changes in temperature caused by the discharge of heated effluents, or global warming, can interfere with this process (Dallas and Rivers-Moore, 2013).

2.6.2 Dissolved oxygen

Dissolved oxygen (DO) in natural waters varies diurnally, exhibiting low values at dawn and increasing concentrations during the day, particularly mid-afternoon. These variations are due to the uptake of oxygen during respiration by aquatic organisms and the process of photosynthesis undertaken by plants (Dallas and Day, 2004). During summer, DO levels are generally lower than in other seasons because DO decreases with an increase in temperature (Dallas and Day, 2004; Rossouw et al., 2005). Besides temperature, DO is also affected by changes in salinity and by photosynthesising organisms in the water. Rapid and drastic changes in DO, and low absolute values, have detrimental effects on aquatic species, even resulting in death (Wetzel, 1983). As to be expected, groundwater generally has lower DO levels than those measured in flowing rivers. According to Younger (2007) DO in groundwater is generally usually between 0 and 3 mg/L, with the exception of shallow permeable aquifers that may exhibit DO values has high as 12 mg/L.

2.6.3 pH

pH is a measure of acidity or alkalinity, based on the quantity of hydrogen ions within a solution. At a pH less than 7 water is acidic, while at pH greater than 7 water is alkaline (DWAF, 1996). In terms of the acidity or alkalinity of natural waters, it is expected that their pH would be close to neutral, ranging between 6 and 8. Many aquatic ecosystems are affected by low-pH runoff from industrial or mining activities, which can also infiltrate into the ground, compromising the integrity of groundwater as well. Severe changes in pH affect the organisms that live within river systems, altering the rate of ionic exchange within the body, as well as affecting the toxicity of metals in water (Dallas and Day, 2004). Lithology affects the pH and alkalinity of waters, especially groundwater. Natural groundwater therefore generally has a pH close to 7, and the alkalinity is mostly dominated by bicarbonate ions. Furthermore, biological activities such as photosynthesis, and anthropogenic activities that generate industrial effluent discharge, have the potential to increase or decrease pH values.

According to Raubenheimer and Day (1991) the presence of fynbos vegetation can naturally result in very low pH values in rivers. The presence of fynbos causes the process of acidification to occur, promoting the production of hydrogen ions, thus lowering pH in waters (DWAF, 1996). In this process, secondary plant compounds called polyphenolics, decompose, forming humic and weak organic acids that alter the pH of rivers. In such instances, leachates from fynbos vegetation can considerably lower the pH of waters to values as low as 3.9 (Dallas and Day, 2004). In South Africa such conditions are experienced in the south-western parts of the country (Day and King, 1995; Dallas and Day, 2004).

2.6.4 Electric Conductivity and Total dissolved solids

Total dissolved solids (TDS), refers to the total amount of material dissolved in water, and consists largely of the major ions sodium, potassium, calcium, magnesium, chloride, sulphate and bicarbonate (Dallas and Day, 2004; DWAF, 1996). Electric conductivity (EC) is defined as the capacity of water to conduct a current, and this is made possible by the presence of ions that have an electric charge (DWAF, 1996). TDS and EC are directly proportional to each other (except that TDS includes non-charged organic solutes), and therefore each can be used to estimate the other (Freeze and Cherry, 1979). Naturally TDS is affected by geology and atmospheric conditions, however human activities such as industrial practices and irrigation also have influence. The dissolution of rocks and soils, and to a lesser extent the decomposition of plant material, also contributes to TDS in waters. An increase in TDS can be expected as water flows downstream due to the continuous addition and accumulation of salts from natural and human activities (e.g. return flow from irrigated fields, and industrial and domestic effluents (DWAF, 1996).

In South Africa, considerable variations in EC as a result of variations in geology type exist, for example, rivers that flow over the weathered Table Mountain Group sandstones are characterised by low EC values, while those underlain by Malmesbury Shales that leach more ions exhibit higher EC values. According to Younger (2007), EC in groundwater normally ranges between 15 and 100 mS/m, however in hypersaline or arid regions where highly soluble minerals such as halite are present, or where sea water enters the aquifer, these values can be well exceeded. Ancient deep groundwater in sedimentary basins can have EC values as high as 350 mS/m (Younger, 2007).

2.6.5 Major ions

2.6.5.1 Calcium

Calcium is an essential element for plant and animal growth and is present in natural waters, in the form of minerals on the bed or solutes in the water (Kresic, 2006.). Hardness of water is a direct representation of its calcium (and magnesium) concentrations (DWAF, 1996; Kresic, 2006). A direct relationship between calcium ions and alkalinity exists, waters with very low calcium concentrations generally have a low alkalinity (Day and Dallas, 2004). The solubility of calcium (and magnesium) in water is governed by the carbonate/bicarbonate equilibrium. This degree of solubility is highly dependent on pH (DWAF, 1996).

Calcium ions are dominant in most surface waters (Dallas and Day, 2004). Igneous, feldspar and amphibole rocks contain a substantial amount of calcium but in magmatic formations, calcium concentrations in groundwater are usually low due to the slow rate of the decomposition of the rock minerals. Similarly, calcium concentrations of groundwater associated with metamorphic formations are also low, often less than 100 mg/L (Kresic, 2006). Carbonate sedimentary rocks such as limestone, are usually associated with elevated concentrations of calcium in groundwater as compared to other sedimentary rocks such as sandstones. Although the geological formation in a particular area largely influences the concentrations of calcium, generally concentrations in potable groundwater range between 10 and 100 mg/L, except in regions dominated by limestone and gypsum (Kresic, 2006). Typically, calcium concentrations in fresh water are approximately 10 mg/L and 400 mg/L in sea water.

2.6.5.2 Magnesium

Magnesium is a highly soluble element that is found in chlorophyll and other enzymes (Dallas and Day, 2004), and is vital for the nutrition of plants and animals ((Kresic, 2006). Much like calcium, magnesium also contributes to the hardness of water. In fresh waters, magnesium concentrations generally range between 4-10 mg/L. Magnesium is present in large quantities in magmatic rock minerals such as olivines, pyroxenes, amphiboles and some micas. Magnesium concentrations are usually high in limestone dominated regions. The dissolution of limestones and dolomites results in the presence of magnesium ions in groundwater (Kresic, 2006). Magnesium in water can result in a bitter taste at concentrations above 70 mg/L. An excessive intake of magnesium can lead to health problems such as diarrhoea (DWAF, 1996).

2.6.5.3 Potassium

Potassium is an essential dietary element which generally occurs in water usually in association with chloride. Sources of potassium in waters includes runoff from irrigated lands and domestic wastes. Potassium concentrations in fresh water systems are usually much lower than that of sodium (Dallas and Day, 2004). Typical concentrations of potassium in fresh waters range between 2 and 5 mg/L. According to Kresic (2006) potassium concentrations in groundwater are generally low, particularly in igneous rocks as compared to its abundance in sedimentary rocks. Feldspars and micas are major sources and potassium is also found in association with sodium in many minerals. At high concentrations, a bitter taste in water develops, and consumption can induce nausea and vomiting, however the ingestion of relatively large quantities of potassium is harmless in healthy adults (DWAF, 1996).

2.6.5.4 Sodium

Sodium is a highly soluble element that significantly contributes to salinity. Generally, sodium does not precipitate during evaporation except when saturation occurs, as a result waters in arid regions that receive low rainfall tend to contain elevated sodium concentrations (DWAF, 1996). Sodium (and chloride) become dominant in waters, when calcium and magnesium ions precipitate out of solution (Gibbs, 1970). In the south-western Cape region of South Africa, the main source of sodium ions (and chloride) is rainfall (Day and King, 1995). Sodium is present in waters due to the weathering of sodium bearing rocks, halite dissolution, sea water intrusions, agricultural and domestic return flows (Laar, 2018). Using water that is sodium-rich for the irrigation of crops poses a threat to crop production as it replaces magnesium and calcium ions and damages the soil structure (Kresic, 2006). The excess intake of sodium can exacerbate certain health conditions, especially in individuals suffering from hypertension, cardiovascular or renal diseases. The sodium intake for infants should be closely monitored as it can result in serious health issues (DWAF, 1996).

2.6.5.5 Chloride

Salinity and chloride have a strong relationship, hence sea water has a chloride concentration of about 19 000 mg/L. Chloride is highly soluble, therefore it easily dissolves in water. Sedimentary rocks usually contain larger amounts of chloride than do magmatic rocks. Sources of chloride in groundwater include the dissolution of minerals, seawater trapped between sediments, evaporation of chloride in rain and snow, and chloride from the atmosphere (Kresic, 2006). Sources of chloride in surface water include, irrigation return flows from agricultural practises as well as sewage and industrial effluents (DWAF, 1996). Groundwater characterised by chloride values exceeding 30mg/L is most likely affected by minerals that leach from rocks or from anthropogenic sources of contaminates (Kresic, 2006).

2.6.5.6 Sulphate

Sulphate ions in water are an oxidised form of sulphur, and usually occur in lower concentrations than the other major anions bicarbonate and chloride. When sulphate ions accumulate in large quantities they form sulphuric acid that negatively affects aquatic ecosystems, significantly dropping pH levels. Although not common in pristine environments, in mining regions water containing large quantities of sulphates and in some cases sulphides may seep through to the surface in the form of acid mine drainage. In the atmosphere, sulphur dioxides, together with nitrogen oxides, are responsible for the generation of acid rain, which significantly alters the chemistry of aquatic ecosystems (Dallas and Day, 2004). Sulphates generally form in the atmosphere as sulphur oxides or as a result of dissolution of sulphate minerals in sedimentary rocks (Kresic, 2006). According to Kumar (2013), the dissolution of gypsum, in particular, in sedimentary deposits and anthropogenic activities make a major contribution towards the accumulation of sulphate in waters.

In groundwater, concentrations of sulphate in regions comprised of magmatic or intergranular sedimentary rocks are usually lower than 30 mg/L. In layered sedimentary deposits, where gypsum and anhydrite are commonly found, sulphate concentrations may even exceed 1000 mg/L. Bacterial reduction in groundwater significantly limits the concentration levels of sulphate, yielding sulphate values that can be as low as zero (Kresic, 2006). In surface water, sulphate concentrations are usually near 5 mg/L, although concentrations of several hundred milligrams per litre may be measured where dissolution of sulphate minerals or discharge of sulphate-rich effluents from acid mining occur. Sulphate imparts a bitter or salty taste to water and the consumption of drinking water containing excessive amounts of this ion may result in diarrhoea.

2.6.5.7 Bicarbonate and carbonate

These ions are a measure of the total alkalinity of a sample of water. In groundwater, these ions are derived from the atmosphere and soils, and from the dissolution of calcium-carbonate-dominated rocks. The dissociation of carbon dioxide into carbonate, bicarbonate and hydrogen ions is largely dependent on pH. The dissolution process of bicarbonate into carbonate usually only begins at a pH of 8.35 (Kresic, 2006). Day and King (1995) and Dallas and Day (2004) further explained that in waters with a pH lower than 8.4, it can be assumed that dissolved inorganic carbon is present only in the form of bicarbonate. Bicarbonate in groundwater generally ranges between 50-400 mg//L, however in regions where fault and metamorphic zones are present the concentrations of bicarbonate tend to be higher, in some cases even exceeding 1000 mg/L.

2.6.6 Nutrients

Nutrients play a major role in the functioning and well-being of plants. Although imperative for plant growth, an excess of nutrients can also be problematic. In natural waters, nitrate and phosphate ions are generally present in low amounts, however they are artificially increased by anthropogenic sources. Dallas and Day (2004) identified activities that are prone to increase nutrient enrichment. They include poor agricultural practices that use excessive quantities of fertiliser; urban runoff; discharge from waste water treatment plants and sewage waters from nearby settlements as well as effluents from livestock farming. Although agriculture has previously been identified as the leading cause of nutrient enrichment, other activities mentioned above also contribute significantly.

Rivers in dry regions often exhibit variable nutrient concentrations from season to season (Lillebø et al., 2007). The relationship between river discharge and nutrient concentrations is often responsible for these variations (Britton et al., 1995). Streams in arid and semi-arid regions, which are usually non-perennial due to low amounts of rainfall and high evaporation rates, are subject to excess nitrogen, especially in its organic form (Arce et al., 2015). The transformation of nitrogen in temporary streams is highly variable due to their unpredictable flow regimes (Scholz et al., 2002). During the dry season, pools that form within the river channel often serve as transport mechanism for nutrients. According to Arce et al. (2015) nutrients and sediments can be transferred between pools that are hydrologically connected. Floods, which are common in these systems, also flush nutrients into the river, drastically increasing nutrient concentrations and also altering other aspects of water chemistry. Lillebø et al. (2007) investigated on the dynamics of nutrient concentrations in a seasonal stream and confirmed that the process of re-wetting following a period of no flow is the most important factor controlling nutrient concentrations in temporary rivers.

2.7 Hydrogeochemical processes

Groundwater chemistry is affected by factors such as the medium through which the water flows, residence time, amount and composition of rain, evapotranspiration, sea water influences and biological processes that occur in the subsurface zone (Hiscock, 2005). In semi- arid regions, evaporation and rock-water interactions are usually the dominating hydrogeochemical process influencing groundwater chemistry. Evaporation in particular, may be prominent in groundwater if water levels are shallow. The process of dissolution in groundwater usually includes minerals such as calcite, dolomite, gypsum and halite, however calcite dissolution is the most common (Kumar et al., 2016). Elango and Kannan (2007) further emphasised that generally, rock-water interactions are the major processes that characterise the chemistry of groundwater primarily because organic and inorganic matter serve as both sinks and primary sources of dissolved solutes in groundwater.

2.7.1 Methods for hydrogeochemical characterization

Hydrogeochemical facies can be determined using various graphical representations such as Piper, stiff and Durov diagrams. These diagrams give insight into water types and chemical processes controlling the water chemistry of water sources. According to Hiscock (2005), to understand the influence of hydrogeochemical processes on water chemistry, the generation of diagrams that identify hydrogeochemical facies using chemical data is useful. The application of characterization tools, such as stoichiometric analysis and bivariate correlation plots, can be used for the analysis and interpretation of hydrochemical data, which involves the identification of geochemical processes that influence groundwater chemistry.

2.7.1.1 Piper diagrams

Piper diagrams, proposed by Piper (1944), are widely used for the indication of major water types and the chemical evolution or origin of groundwater (El-Manharawy and Hafez, 2003; Kumar, 2013). They categorize water samples, based on their cation and anion proportions in percentages of milliequivalents per litre. These diagrams classify water into one of six major categories, namely, Ca-HCO_3, Na-Cl, Ca-Mg-Cl, Ca-Na-HCO_3, Ca-Cl and Na-HCO_3 type (Kumar, 2013).

According to Kumar (2013), the evaluation of water type provides information necessary in understanding hydrochemical processes that occur within the subsurface. Piper diagrams are useful because they can plot and represent a number of different water types on one diagram, although this diagram does not show differences in ionic concentrations between samples. As a result, concentrated and dilute samples may fall in the same position despite vast differences in ionic compositions (Bredenhann and Hodgson, 1998; Ligavha-Mbelengwa, 2017). Several studies (Kumar, 2013; Manoj et al., 2013; Kumar, et al., 2016; Laar, 2018) have utilized piper diagrams as tools for the characterization of groundwater chemistry in different regions of the world.

2.7.1.2 Stoichiometric analysis

Stoichiometric analysis provides the relationship between variables in the form of reactants and products in a balanced chemical reaction. This analysis is based on calculations of groundwater reactions that can be used to assess the hydrogeochemical processes taking place. According to Hounslow (1995), as groundwater moves from areas of recharge at higher gradients to lower gradient discharge areas, processes such as evaporation and the weathering of rocks undergo reactions that alter groundwater chemistry by producing different minerals during the reaction. These reactions, known as stoichiometric reactions, also give an indication of the origin of groundwater (Ligavha-Mbelengwa, 2017). According to Carol and Kruse (2012) and Laar (2018), chemical reactions that take place within the subsurface are responsible for the occurrence and abundance of dissolved ions in groundwater.

2.7.1.3 Bivariate correlation

Bivariate correlation is applied to measure the strength of the relationship between two variables. The strength of the relationship is provided by the correlation coefficient value (R^2) between 0 and ±1 based on the generated scatter plot (Acock, 2008; Ligavha-Mbelengwa, 2017). A strong relationship between two variables is represented by an R^2 value close to 1, while a weak relationship is depicted by an R^2 value close to 0. According to Mackenzie and Garrels (1971), bivariate correlation plots are useful in showing outliers that would otherwise reduce the strength of the relationship between two variables. Although a useful and easy tool to interpret hydrochemical data, bivariate plots can generate inaccurate results. A small data set may be misleading, allowing relationships between variables to appear linear with a strong r value when in fact the relationship is of a non-linear nature.

A considerable number of studies (e.g. Solomon, 2013; Kumar et al., 2016; Ligavha-Mbelengwa, 2017; Laar, 2018) applied bivariate correlation for the analysis of hydrochemical data and the identification of hydrogeochemical process that influence groundwater. Solomon (2013) and Laar (2018) generated bivariate correlation plots of hydrochemical data to understand and determine the influences of precipitation, evaporation and rock–water interactions on groundwater. Data analysis included scatter plots of various combinations of major ions, for example those for EC vs. Cl^- , Cl^- vs. Na^+, (Ca^{2+} + Mg^{2+}) vs. (HCO_{3-} +SO_4). Laar (2018) identified sea water intrusion and weathering of silicate mineral as the main hydrogeochemical processes controlling groundwater chemistry of the wetland and groundwater quality in the Sakumo Wetland basin in Ghana.

2.8 Environmental Isotopes

As fresh water resources continue to deplete in quantity and deteriorate in quality, disciplines such as isotope hydrology are on the rise (Deodhar et al., 2014). Environmental isotopes can be used as confirmatory tools to complement geochemistry in the assessment of water chemistry (Clark and Fritz, 1997). Hydrological processes such as groundwater- surface water interactions can be established using isotopes as tracers. Variations in stable isotopes can be used to determine sources of groundwater recharge and processes, origin and age of groundwater, rock-to-water interactions, geochemical evolution, origin of salinity, and contamination (Laar, 2018).

Isotopes of the water molecule (^{18}O and ^{2}H), which the current study used as tracers are particularly useful as they form as a result of meteoric water within the catchment. According to Laar (2011) these tracers are unique because their composition is not usually altered by the medium through which water flows (groundwater material) or by other elements of the water cycle. Meteoric processes alter the isotopic signature of water molecules, resulting in recharge with a distinctive isotope signature. ^{18}O and ^{2}H in precipitation provide a characteristic signature that allows for the tracing of groundwater recharge. This signature varies spatially and temporally. The isotopic composition of precipitation during the rainout process is therefore largely controlled by temperature (Clark and Fritz ,1997). Craig (1961) observed that the isotopic composition of meteoric water had a predictable pattern. Cold regions were characterised by isotopically depleted water while enriched isotopic compositions were identified in warmer regions.

The composition of hydrogen and oxygen isotopes is affected by hydrological processes such as evaporation, condensation and melting that takes place on the surface as well mixing that occurs at or below the ground. Changes in these compositions allow for the origin of water to be determined (Craig, 1961). Uses of stable isotopes in water chemistry also include determining sources of solutes, and the effects of precipitation on water chemistry. Solutes from different origins (precipitation, geology, anthropogenic) exhibit distinctively different isotopic signatures.

2.8.1 Isotope fractionation

Generally, lighter isotopes of the water molecule will evaporate first, while heavier isotopes are likely to condense first (Deodhar et al., 2014). Ratios of the same isotope e.g. (O-16 and O-18) differ slightly, either due to preferential diffusion of lighter or heavier isotopes or though the preferential location that is associated to bond energies that are related to mass. This process is known as fractionation. Isotope fractionation can be either kinetic or equilibrium. Drivers of isotope fractionation include chemical and physical reactions, diffusion and exchange. Kinetic fractionation occurs when molecules and atoms consisting of different isotopes proceed through these reaction processes at different rates. If these reactions are permitted to run to completion, allowing for reactions to continue at an equal rate backward and forward at a certain temperature, equilibrium is reached. A fixed isotope difference is therefore achieved between the source and the receptor (Diamond, 2014). Isotope fractionation is largely influenced by temperature and the degree of fractionation tends to be less at high temperatures. Although the process of fractionation does not significantly affect variations in isotope compositions, the relationship between ^{18}O and ^{2}H arises from this process. Rayleigh distillation that occurs during rainout results in the differences exhibited by ^{18}O and ^{2}H in warm and cold regions (Clark and Fritz, 1997).

2.8.2 The relationship between 18O and 2H

The ratio of isotopes is expressed as the heavier, less abundant, isotope to the lighter, more abundant, isotope. The true or absolute isotope ratio cannot easily be measured therefore the apparent ratio measured by mass spectrometry is used instead (Clark and Fritz, 1997). Isotope concentrations are expressed as the difference between the measured ratio of the sample and the reference over the measured ratio of the reference denoted as:

$$\delta^{18}\,O_{\text{sample}} = \frac{m(^{18}O/^{16}O)_{\text{sample}} - m(^{18}O/^{16}O)_{\text{reference}}}{m(^{18}O/^{16}O)_{\text{reference}}} \tag{2.1}$$

Isotope compositions of water are expressed as parts per mil difference from the reference, denoted as ‰. This reference is known as the Vienna Standard Mean Ocean Water (VSMOW) standard, an internationally agreed sample of ocean water. The isotope compositions of Oxygen-18 and deuterium (^{18}O and ^{2}H) were denoted as $\delta^{18}O$ and $\delta^{2}H$. Water with less $\delta^{18}O$ and $\delta^{2}H$ than VSMOW has negative values, while water with more $\delta^{18}O$ and $\delta^{2}H$ than VSMOW is represented by positive values (Laar, 2018).

To define the relationship between $\delta^{18}O$ and $\delta^{2}H$, Craig (1961) established a reference for interpreting the provenance of groundwater. The Global Meteoric Water Line (GMWL) developed by Craig (1961) together with Dansgaard (1964) defines the relationship between $\delta^{18}O$ and $\delta^{2}H$ and worldwide precipitation values. According to Clark and Fritz (1997) the GMWL is based on global averages of local meteoric water lines that are affected by local factors such as climate that influence the deuterium excess and slope values. The GMWL is based on the Equation:

$$\delta^{2}H = 8 \times \delta^{18}O + 10 \text{ ‰ VSMOW} \qquad (2.2)$$

2.8.3 Deuterium excess of meteoric water

Craig's meteoric line has a deuterium excess (d-excess) of 10, which generally corresponds to the global average. This is because global atmospheric water vapour forms at an average humidity and produces precipitation that is displaced by 10 for $\delta^{2}H$ from seawater. Regionally d-excess values vary primarily due to variations in humidity or due to differences in the rate of rainfall evaporation. Other contributing factors such as wind speed and sea surface temperatures influence the d-excess value (Clark and Fritz, 1997). High d-excess intercepts generally occur in regions characterised by fast evaporation rates and where rainfall is evaporated (Laar, 2018).

The deuterium excess of global precipitation is expressed as "d" for a slope of 8 and can be expressed as:

$$d = \delta^{2}H - 8\delta^{18}O \qquad (2.3)$$

2.8.4 Factors that influence isotope compositions

According to Craig (1961) stable isotopic composition of precipitation are influenced by the latitude effect, seasonal effect, continental effect and altitude effect.

Latitude effect: A depletion in $\delta^{18}O$ and $\delta^{2}H$ values is expected with an increase in latitude (Clark and Fritz 1997). Regions at low latitudes therefore have more positive $\delta^{18}O$ and $\delta^{2}H$, while regions at higher latitudes are characterised by negative $\delta^{18}O$ and $\delta^{2}H$ values. Decreases in $\delta^{18}O$ and $\delta^{2}H$ can be expected with distance from the equator (Laar, 2018).

Continental effect: Isotope composition of precipitation near the coast are more enriched, while inland regions are characterised by more negative and depleted $\delta^{18}O$ and $\delta^{2}H$ values. Compositions of $\delta^{18}O$ and $\delta^{2}H$ generally decrease with distance from the coast. As vapour masses travels from the ocean where it originates, across a continent, effects of topography and temperature influence the isotopic composition. Air masses undergo condensation near the coast, releasing enriched $\delta^{18}O$ and $\delta^{2}H$ isotopes. A decrease in heavy isotopes occurs as the air mass travels inland (Clark and Fritz, 1997).

Altitude effect: Compositions of $\delta^{18}O$ and $\delta^{2}H$ decrease with an increase in altitude. Temperature and topography largely influence the magnitude of the altitude effect. High altitude areas are characterised by lower temperatures, therefore the depleted nature of isotope composition in these regions are also related to decreases in temperature. The depletion of $\delta^{18}O$ varies between -0.15 and -0.5 ‰ and of $\delta^{2}H$ between -1 and -4 ‰ per 100 m increase in altitude. The altitude effect is useful for distinguishing groundwater recharged at high or low altitudes (Clark and Fritz, 1997).

Seasonal Effect: Seasonal **v**ariations in temperature influence the composition of $\delta^{18}O$ and $\delta^{2}H$. During periods of high average temperatures, positive enriched $\delta^{18}O$ and $\delta^{2}H$ values are expected, while negative depleted values of $\delta^{18}O$ and $\delta^{2}H$ are expected during periods of lower average temperatures. Seasonal fluctuations are more prominent inland, while seasonal variations near the coast are limited. Seasonal variations are minimal in groundwater due to confinement e.g. confined aquifers. Seasonal effects are therefore more pronounced in surface water than in groundwater (Clark and Fritz, 1997).

2.9 A review of previous water chemistry studies in South Africa

Several investigations (Noble and Hemens, 1978; Silberbauer and King, 1991; Jones et al., 2000; Russell and Impson, 2006) on the water chemistry of surface waters on the Agulhas plain, particularly focused on wetlands have been conducted. These studies primarily reported on the physical and chemical properties of waters, such as pH, EC, DO and nutrient concentrations. Comprehensive water quality studies on the chemistry of rivers and aquifers that quantify and assess variable water quality parameters within the region are, however, generally lacking, although some attempts to quantify physical parameters of surface waters have been recently undertaken.

Studies by Mazvimavi (2017) and Kraaij et al. (2009) reported on the general water quality condition of rivers on the Agulhas plain. In particular, Mazvimavi (2017), among other aspects, investigated on the water quality of surface waters within the Nuwejaars Catchment, in an attempt to address water demands within the Catchment. Although detailed hydrochemical data was not collected, in-situ parameters EC, pH and DO were measured during 2014 and 2015. This study reported on increasing pH values from upstream to downstream, with tributaries of the Nuwejaars River, recording pH values that are indicative of acidic waters. Results also suggested that Wetlands (Soetendalsvlei and Voëlvlei) within the catchment, through which the Nuwejaars River flows, did not significantly affect the pH values recorded during the duration of this study. Kraaij et al. (2009), had previously also described rivers on the Agulhas plain as consisting of alkaline and brackish waters, however, with pH values ranging between (4.5 to 5.0) in the uplands. According to Mazvimavi (2017) dissolved oxygen concentrations were variable during 2014 and 2015, however increased concentrations in the upper tributaries and after Soetendalsvlei were reported on. Furthermore, low EC values in the uplands of the catchment, with an increase in EC further downstream, particularly after Voëlvlei were recorded during 2014-2015. EC values were reported as highly variable across the catchment, although the highest values were recorded during the drier months of January- May 2015 when less rain was received.

Day and King (1995) investigated on the proportions of major ions in South African rivers. Four broad categories that represent waters of different ionic proportions were identified. The categories were: 1) river waters dominated by Ca^{2+}, Mg^{2+} and HCO_3^- and situated inland in the east-central highlands 2) rivers surrounding the east-central highlands and dominated by Ca^{2+}, Mg^{2+} and Na^+, with HCO_3^- 3) rivers in the mid-west with waters roughly equimolar for both anions and cations, and 4) saline coastal rivers situated in the south-west dominated by $Na^+$and Cl^-. According to the categories stipulated by Day and King (1995), The Nuwejaars Catchment, the study area of the current study falls under category 4.

Seaman et al. (2010) investigated nutrients in pools in the Seekoei River in the Free State. They found no clear trends, however some seasonal patterns were established: e.g. dissolved organic nitrogen increased during winter months while dissolved organic phosphorus decreased. In pools, algal species diversity was found to be higher in warmer months than in winter months. On the Agulhas plain, wetland waters were reported to consist of variable nutrient concentrations, ranging from nutrient rich to nutrient poor waters. In particular, according to Kraaij et al. (2009) the wetland Soetendalsvlei, through which the Nuwejaars River flows consists of waters with the high nutrient concentrations (phosphorus and nitrogen). It can, therefore, be expected that the Nuwejaars River after Soetendalsvlei may contain high concentrations of nutrients as compared to the upland areas of the catchment.

In a local study conducted by Conrad et al. (1999) on behalf of the South African Water Research Commission, it was concluded that shallow unconfined or semi-confined aquifers are mostly vulnerable to contamination in agricultural regions, water quality of shallow aquifers is significantly altered by the infiltration of agricultural and livestock effluents. Meanwhile, Ncube and Schutte (2005) reported on the general status of groundwater in South Africa, concluding that groundwater in South Africa is generally of an acceptable quality although water quality constitutes such as fluoride, nitrates, heavy metals, sulphates and total dissolved solids were found to be elevated in some regions.

Wu (2008) investigated on the occurrence of groundwater in the Table Mountain Area of Cape Town. To achieve this, the effects of topography on groundwater flow and groundwater quality were assessed. After quantifying various physical and chemical constitutes of groundwater, Wu (2008) reported that groundwater in the TMG region is of a high quality, with low salinities, rarely exceeding 100 mS/m. Furthermore results indicated that groundwater within this region was slightly acidic, with pH values ranging between 4.7 and 6.2.The values were consistent with areas that fall under the Fynbos biome. Wu (2008) further classified the Table Mountain Spring as being dominated by sodium and chloride, concluding that groundwater quality in the Table Mountain area is primarily affected by topography, lithology, and the climatic conditions of the region.

2.10 Theoretical Framework

The theories of dilution, dissolution and mineralization are used to explain the chemistry of surface and groundwater. Water quality in surface and groundwater is naturally influenced by geological, topographical, meteorological, hydrological and biological processes. The influence of these processes on water quality are more pronounced in regions that receive low amounts of rainfall. In semi-arid regions characterized by low rainfall amounts and high evaporation rates, evaporates tend to leach into the saturated zone reducing the effects of dilution in groundwater. These conditions also have a pronounced effect on the dilution of solutes in rivers (von Schiller et al., 2011). The process of dilution in N-PRs is generally limited due to low quantities of water within the river. Changes in water quality can be expected in N- PRs as a result of their variable flow conditions (Rossouw et al., 2005).

Groundwater quality is primarily influenced by the composition of the recharge water, the composition of the aquifer material through which it flows and the reactions that take place within the aquifer. The process of mineralization that influences groundwater chemistry is largely dependent on the composition and solubility of the rocks, and the residence time of groundwater. The residence time of groundwater determines the duration in which groundwater reacts with the aquifer material. High contact time, promotes rock–water interactions which elevate dissolved ions in groundwater. The rate of groundwater flow determined by hydraulic gradients influences the mineralization of groundwater (Elango and Kannan, 2007).

Chapter 3: Description of study area

This chapter provides a description of the study area in terms of location, climate, geology, vegetation and other land use activities within the catchment. This description includes spatial maps that show differences in geology and land use type across the catchment .The description and locations of the groundwater and surface water sampling points selected for this study are also provided.

3.1 Location and topography

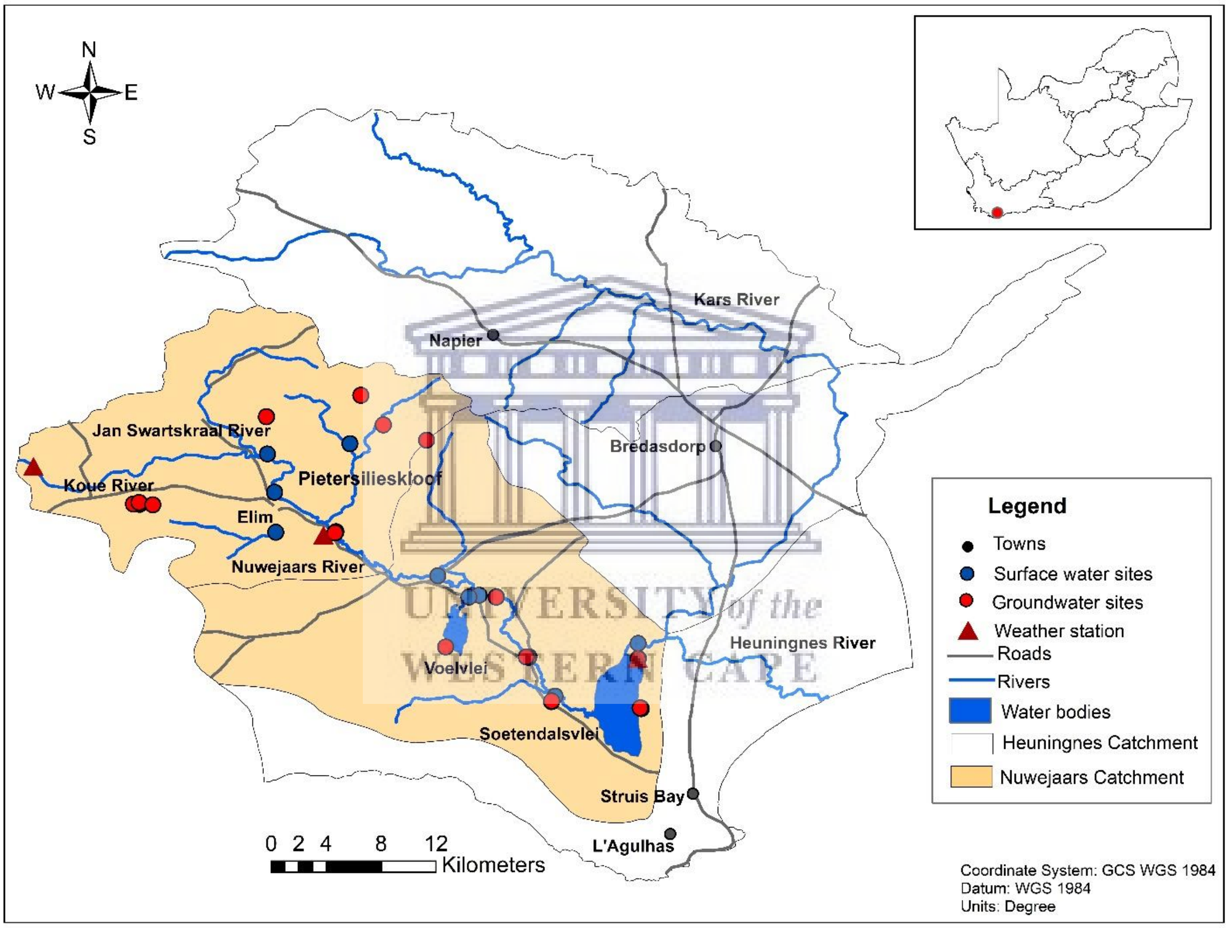


Figure 2a: Study area map of the Heuningnes Catchment and the Nuwejaars Quaternary Catchment (G50B and G50C) with groundwater and surface water sampling points

The Nuwejaars Catchment located in Cape Agulhas near the southern-most tip of Africa, covers a total area of 760 km^2. The catchment falls under the Overberg-east region within the Western Cape province of South Africa. It consists of quaternary catchments G50B and G50C, as assigned by the Department of Water and Sanitation (DWS) and falls within the Breede-Gouritz Water Management Area (BGCMA).

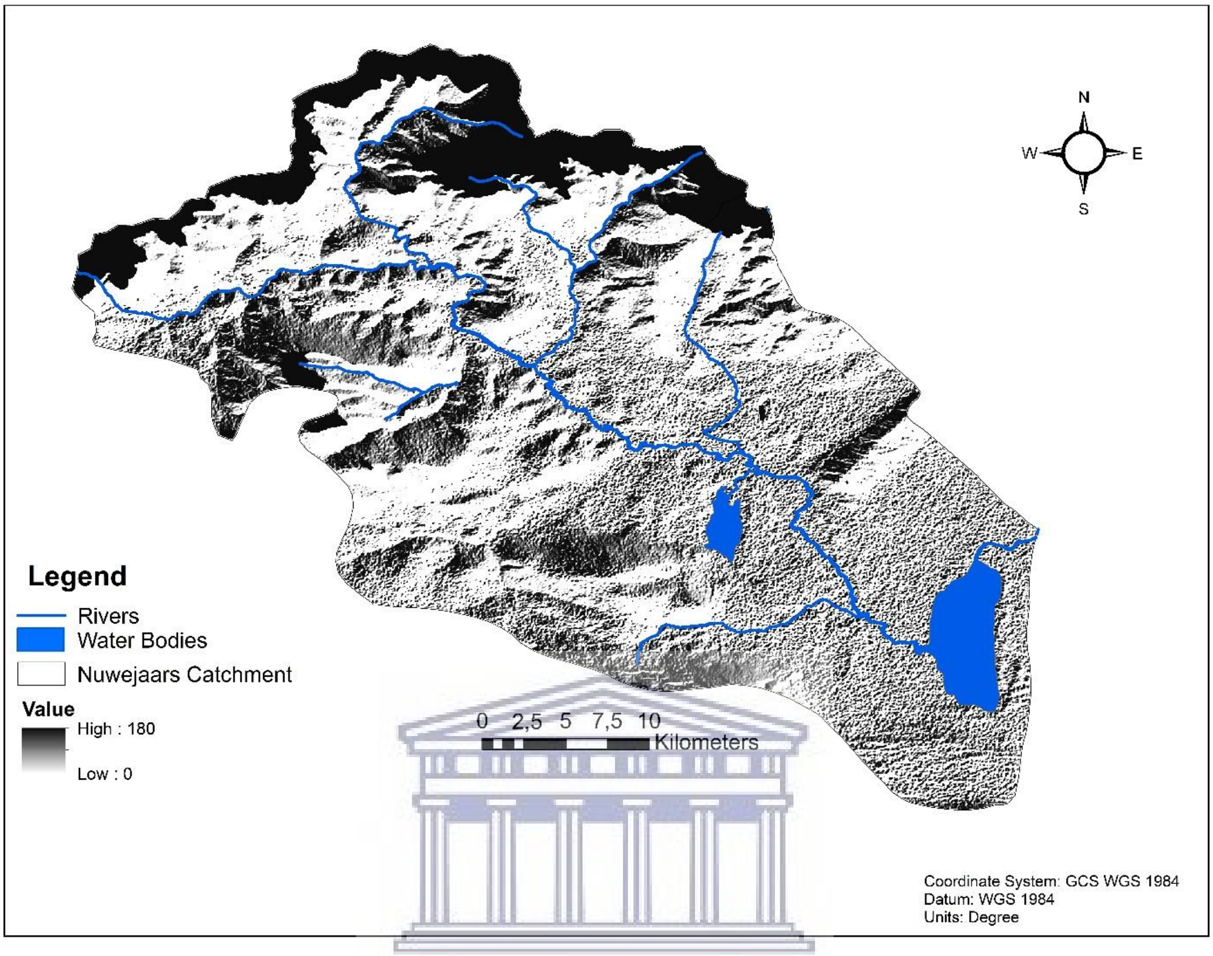


Figure 2b: Topography map of the Nuwejaars catchment (quaternary catchments G50B and G50C).

The head waters of the catchment are located in the Koue and Bredasdorp Mountains, which reach an altitude of 650m. The majority of the catchment, particularly quaternary catchment G50C, is low-lying with an altitude ranging between 5 and 60m above sea level. The catchment is characterised by a rapid decrease in altitude from the headwaters to the main tributaries in the low lying sections of the catchment (Mazvimavi, 2017). Surrounding towns include Elim, Bredasdorp, Struisbaai, Napier and L'Agulhas (Kraaij et al., 2009; River Health Programme, 2011). The town of Elim, which falls within the study area (Figure 2a), has a population of 1412 people, whose livelihood depends on the water resources within the catchment (Mazvimavi, 2017).

3.2 Climate

The Nuwejaars Catchment typically receives rainfall throughout the year, although the highest rainfall is received during the winter months (June to August), while the least is received during summer (December to March) (Mazvimavi, 2017). Winter rainfall normally accounts for approximately 75% of the precipitation received within this catchment, while potential evaporation usually well exceeds the mean annual rainfall during the dry season (Cowling et al., 1988; Kraaij et al., 2009). The mean annual rainfall ranges between 445 and 540 mm from east to west along the coast of the Agulhas Plain (Kraaij et al., 2009), 455mm in the lower sections of the catchment and 600mm in the mountainous recharge area, upstream (Mazvimavi, 2017). The average maximum temperatures during summer and winter are approximately 25°C and 18 °C, respectively (Mazvimavi, 2017).

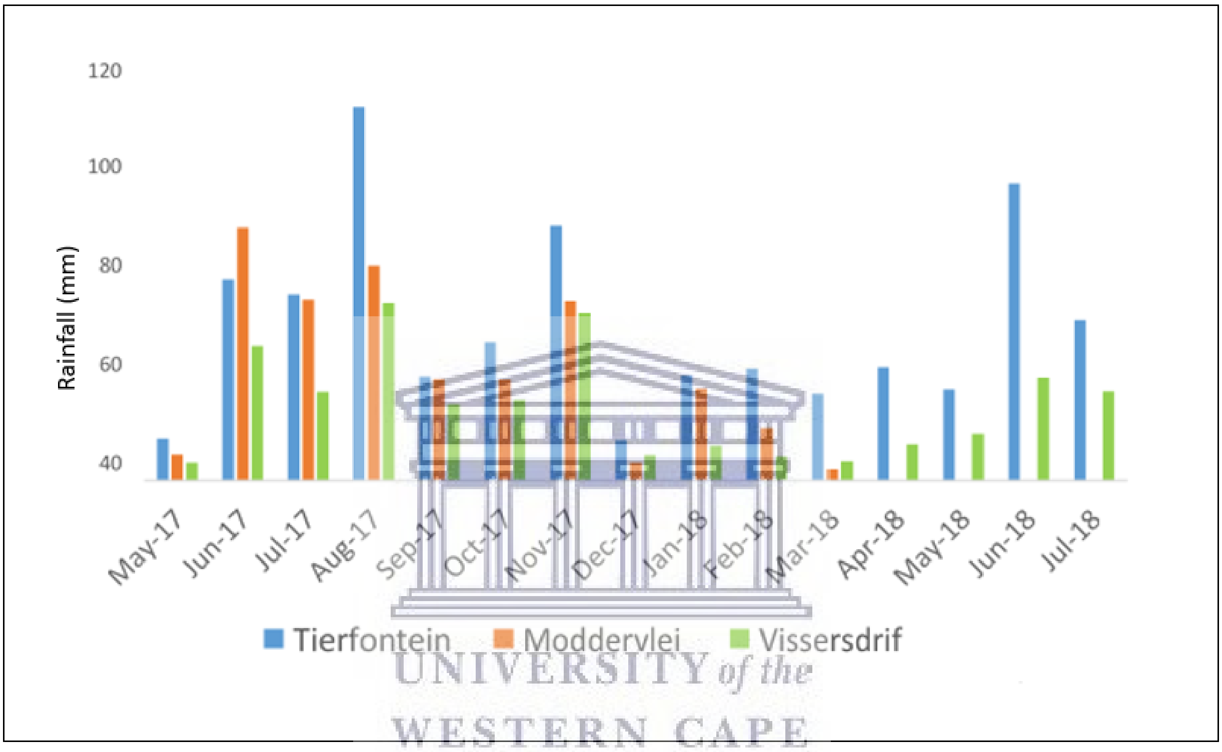


Figure 3: Total monthly rainfall received within the Nuwejaars Catchment during May 2017-July 2018 ***(****rainfall data obtained from UWC weather stations****).***

The total monthly rainfall recorded during the study period, at 3 stations, Tierfontein (upstream), Moddervlei (mid-catchment) and Vissersdrif (downstream), are presented in Figure 3. The location of the weather stations are represented in Figure 2a (study area map). Peaks can be observed during June and August in 2017 and a decrease from September 2017 to March 2018. Rainfal increases during the wet season of 2018 can also be observed. The weather station in the recharge area of the catchment (Tierfontein), recorded the highest amount of rainfall, throughout the catchment. According to Mazvimavi (2017), the drought experienced during 2017 particularly affected the southern parts of the catchment, which received only half of the mean annual rainfall recorded in previous years.

3.3 Hydrology

In the upper reaches of the catchment, the Koue and Jan Swartskraal rivers join to form the Nuwejaars River. Other tributaries of the Nuwejaars River include, Pietersielieskloof, Voelvlei and Bloomkraal rivers in the lower western sections of the catchment. The Nuwejaars River flows into Soetendalsvlei, the largest freshwater lake in South Africa, which is 3 km wide and 8 km long, and which then joins the Heuningnes Estuary before discharging into the Indian Ocean (Russell and Impson, 2006; Kinoti, 2018). The catchment is well known for its ecological value; in particular, the Heuningnes Estuary is a Ramsar site that serves as breeding grounds for several endangered bird species and supports a wide biodiversity (Bickerton, 1984; Mazimavi, 2017).

A considerable number of seasonal and permanent wetlands and pans, including Voelvlei, Soutpan, Melkbospan and Soetendalsvlei, are present over a small area within the low lying sections of the catchment (Jones et al., 2000; Kinoti, 2018). These wetlands are habitat to many rare bird and aquatic species, some unique to this area (River Health Programme, 2011; Malan et al., 2015). Soetendalsvlei and Voelvlei, which are usually inundated all year round, are connected to the Nuwejaars River, while the surrounding temporary and hypersaline pans (Soutpan, Melkbospan) are not (River Health Programme, 2011; Kinoti, 2018).

3.4 Groundwater

According to Mazvimavi (2017) a connection between groundwater and surface water exists in the upper reaches of the catchment. Springs upstream that provide water from deep aquifer systems are a source of constant base flow for the Koue, Pietersielieskloof and Jan Swartskraal tributaries. On the other hand, due to low-yielding geological formations and low gradients downstream, groundwater and surface water in the lower sections of the catchment are poorly connected.

The catchment consists of both primary and secondary aquifers. Primary aquifers within the catchment are characterised by unconsolidated sediments deposited during sea level changes and occur at a depth of 8 and 30m. Secondary aquifers within the catchment consist of fractured bedrock and are semi-confined. Groundwater flow within the catchment is controlled by the recharge areas underlain by Table Mountain Group (TMG) formations and existing fault systems. Springs upstream that occur within the TMG region of the catchment and are closely linked to fault systems. These springs are a valuable source of fresh water. They supply the town of Elim with water for domestic use all year round and feed rivers during the dry season. Springs in the upper catchment also provide water for irrigation purposes Mazvimavi (2017). The relationship between groundwater and surface water sampling points is presented in the study area map (Figure 2a).

3.5 Vegetation

Vegetation types and their spatial extent in the Nuwejaars Catchment are presented in Figure 4 (Land-use map).The study area situated on the Agulhas Plain, falls within the Cape Floristic Region, a protected plant rich area located in the Western and Eastern Cape Provinces of South Africa. Areas within the Cape floral region are protected biodiversity hotspots that consist of various endemic vegetation types (Blokker et al., 2015). These vegetation types include natural shrublands that consist of unique fynbos species. According to Cowling and Mustart (1994) and Kraaij et al. (2009) the Agulhas National Park, consists of more than 1750 plant species. The largest aerial extent of lowland fynbos in the entire Cape Floristic region, is within the Agulhas plain. Cowling and Mustart (1994) and Cole et al. (2000) reported on 9 broad groups of vegetation types present within the Agulhas National Park, of which 7 out of 9 of these vegetation groups are fynbos eg. Elim asteraceous fynbos.

A large section of the Nuwejaars Catchment has maintained its natural state, with fynbos covering up to 41% of the catchment (Kinoti, 2018). Alien vegetation such as *Acacia* species and eucalyptus trees have invaded the upper reaches of the Nuwejaars catchment, especially along the riparian zone of the river. Agriculture and livestock farming dominate in some areas (Kraaij et al., 2009; Mazvimavi, 2017). Crops cultivated within the catchment include wheat, barley and canola, while vineyards are also present (Russell & Impson 2006; Kinoti, 2018), and continue to extend over larger and larger areas of the catchment. Several livestock farms that breed cattle and sheep are situated near the Nuwejaars River (Mazvimavi, 2017).

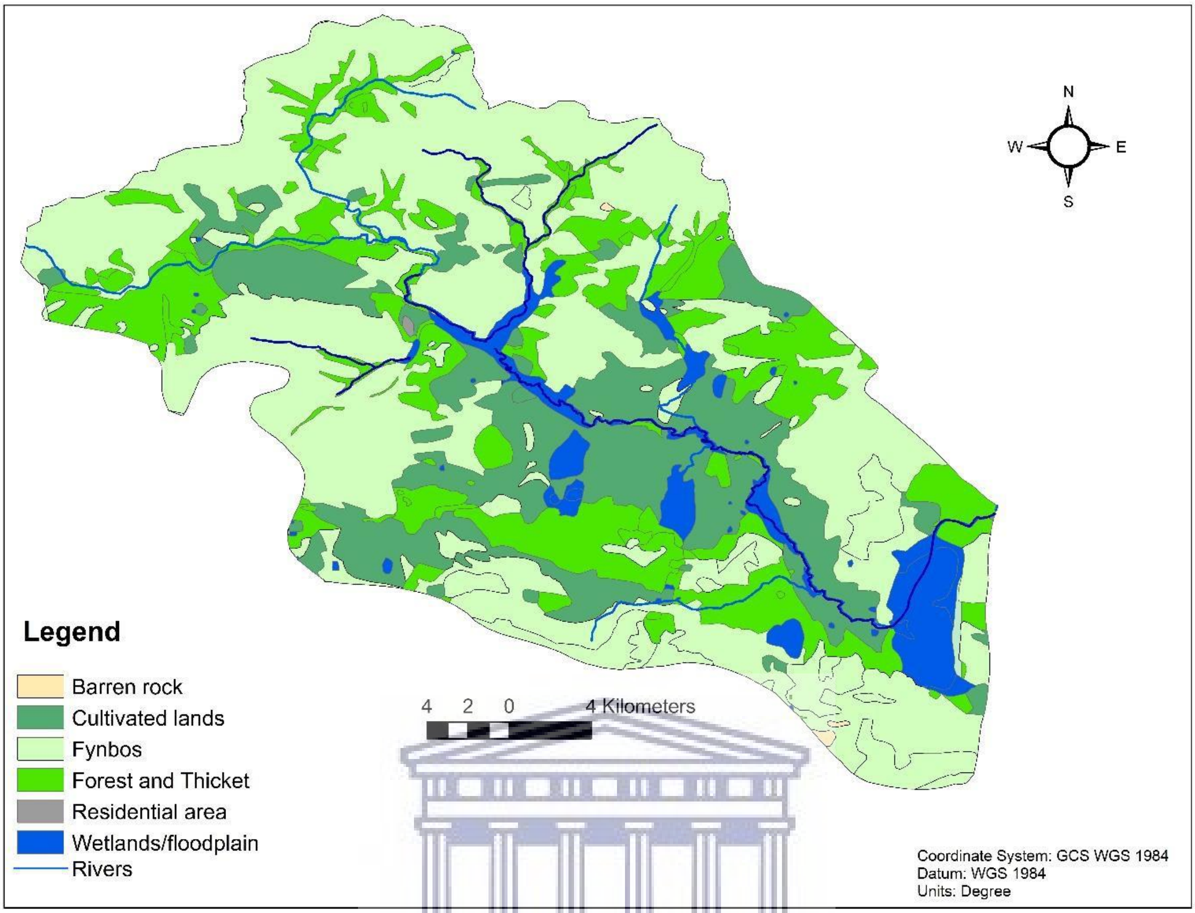


Figure 4: Land-use types within the Nuwejaars Catchment.

3.6 Geology

The study area is dominated by geological formations of the Malmesbury, Table Mountain, Bokkeveld, Cape Granite Suite and Bredasdorp Groups (Kinoti, 2018). Geology types that underlie the Nuwejaars Catchment are presented in Figure 5. The upper sections of the Nuwejaars Catchment are dominated by formations of the Table Mountain Group, which consist of quartzitic sandstones. The Table Mountain Group of the Cape Supergroup was deposited during the Ordovician, Silurian and Devonian period (Roets et al., 2008; Kinoti, 2018).

The Bokkeveld Group, which was deposited during the early to mid-Devonian, dominates in the mid-sections of the catchment and consists primarily of shales and sandstones in an alternating sequence (Kinoti, 2018). The Bokkeveld Group, which covers the largest area within the catchment, lies between the Table Mountain and Bredasdorp Group. The Table Mountain Group upstream and the Bokkeveld Group in the mid sections of the catchment, overlay basement formations of the Malmesbury Group and Cape Granite. Granite outcrops exist and two geological faults run parallel from east to west, south of the Heuningnes Mountains. A number of faults also cut through the Napier and Bredasdorp Mountains in a north- east to south-west and east to north- west direction (Bickerton, 1984).

The Bredasdorp Group is dominant from Soetendalsvlei to the mouth of the Heuningnes River. This formation primarily consists of calcified dune sands and limestones (Kinoti, 2018). The sequence of geological formations within the Nuwejaars catchment can be summarised as quartzitic sandstones of the Table Mountain Group upstream, followed by a transition into the shale and sandy shales of the Bokkeveld Group in mid sections, which transitions into calcified dune sands and limestones of the Bredasdorp Group towards the coast.

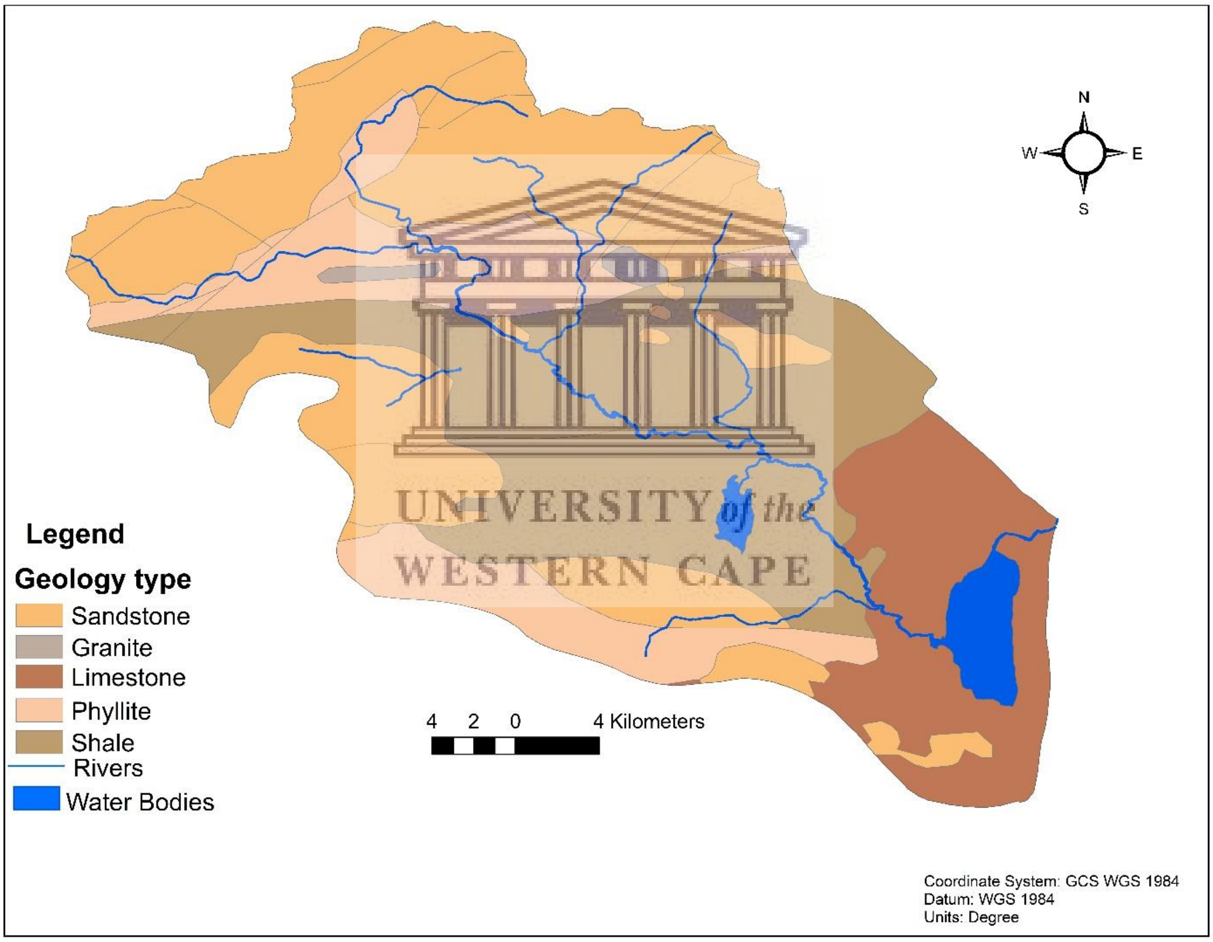
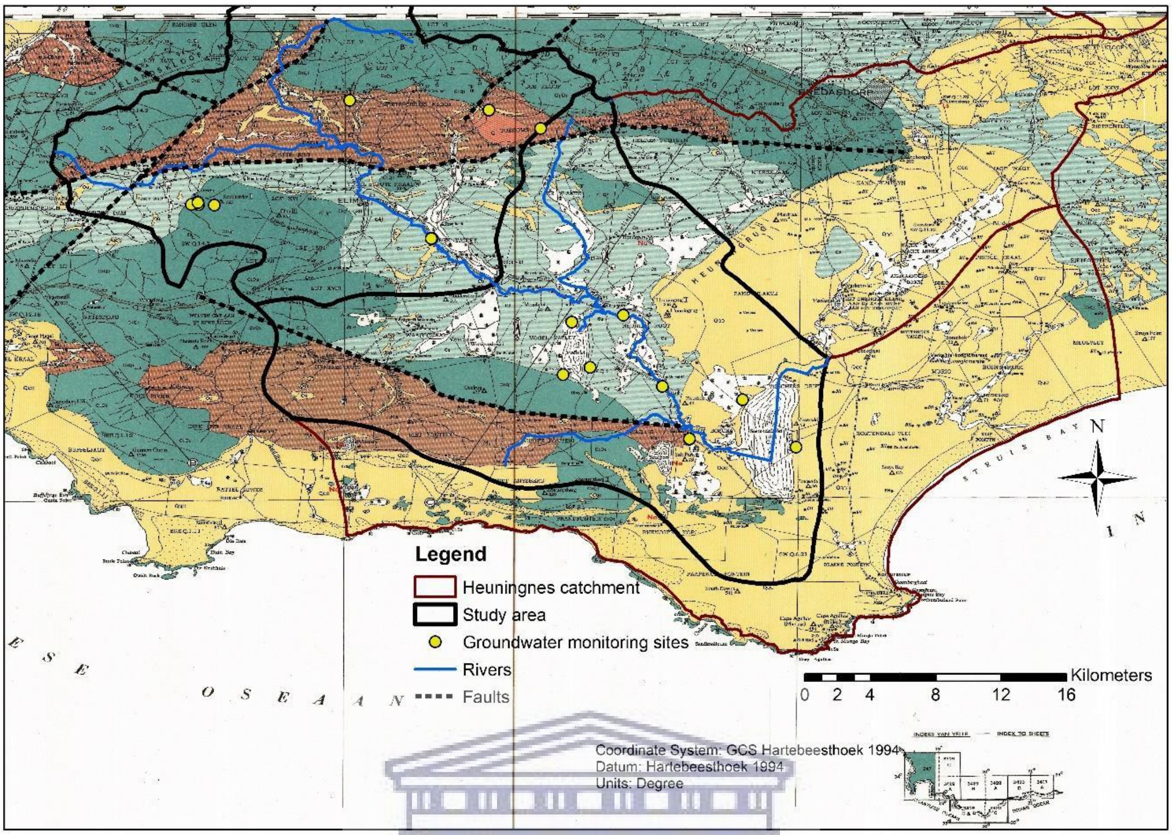


Figure 5a: Geology of the Nuwejaars Catchment.



Source: National Geo-spatial Information

Figure 5b: Location of geological faults within the Nuwejaars Catchment.

3.7 Description and location of the study sites

The number of sampling points varied from season to season during the duration of the sampling period (July 2017-July 2018). Originally, a total of 10 surface water sampling points were selected but these increased to 12 by the third sampling campaign. Due to the nature of N-PRs, sampling for surface water at the selected sites from a flowing river was not always possible. Some samples were collected from pools in sections of the river where they persisted during the dry season.

A total of 24 groundwater sampling points were selected, although the number of groundwater samples differed from season to season. In some cases, boreholes originally selected for the study were inaccessible at the time of sampling, while some piezometers were dry or damaged. As a result gaps are present in the data set, a common occurrence with water quality data. The majority of boreholes and piezometers selected as groundwater sampling points, were drilled for research purposes and are managed by the University of the Western Cape. The criteria for selecting river sites included the following; **I**) location and proximity to accessible boreholes, **II**) dispersion along the river, and **III**) susceptibility and possible vulnerability to land-use activities such as crop and livestock farming. The locations and descriptions of sampling points are presented in Tables 1-3 and Figures 6 and 7.

Table 1: Location and description of surface water sampling points

Site Name	Description of location	Latitude	Longitude
NJ 1	Downstream after Soetendalsvlei	-34.6779	19.9961
NJ 2	Downstream before Soetendalsvlei	-34.7125	19.9417
NJ 3	Downstream at a dairy farm	-34.6867	19.9245
NJ 4	After Voelvlei at a hay field	-34.6475	19.9032
NJ 5	Near Voelvlei outlet bridge	-34.5791	19.7579
NJ 6	At Nuwejaars river bridge	-34.6337	19.8648
NJ 7	At Moddervlei site	-34.6048	19.7981
NJ 8	At Elim bridge upstream	-34.6464	19.8918
VOB	At Voelvlei outlet	-34.6476	19.8852
PT1	Upstream tributary to Nuwejaars River	-34.5472	19.8073
JS1	Upstream tributary to Nuwejaars River	-34.5540	19.7532
ETS	Upstream tributary to Nuwejaars River	-34.6053	19.7587

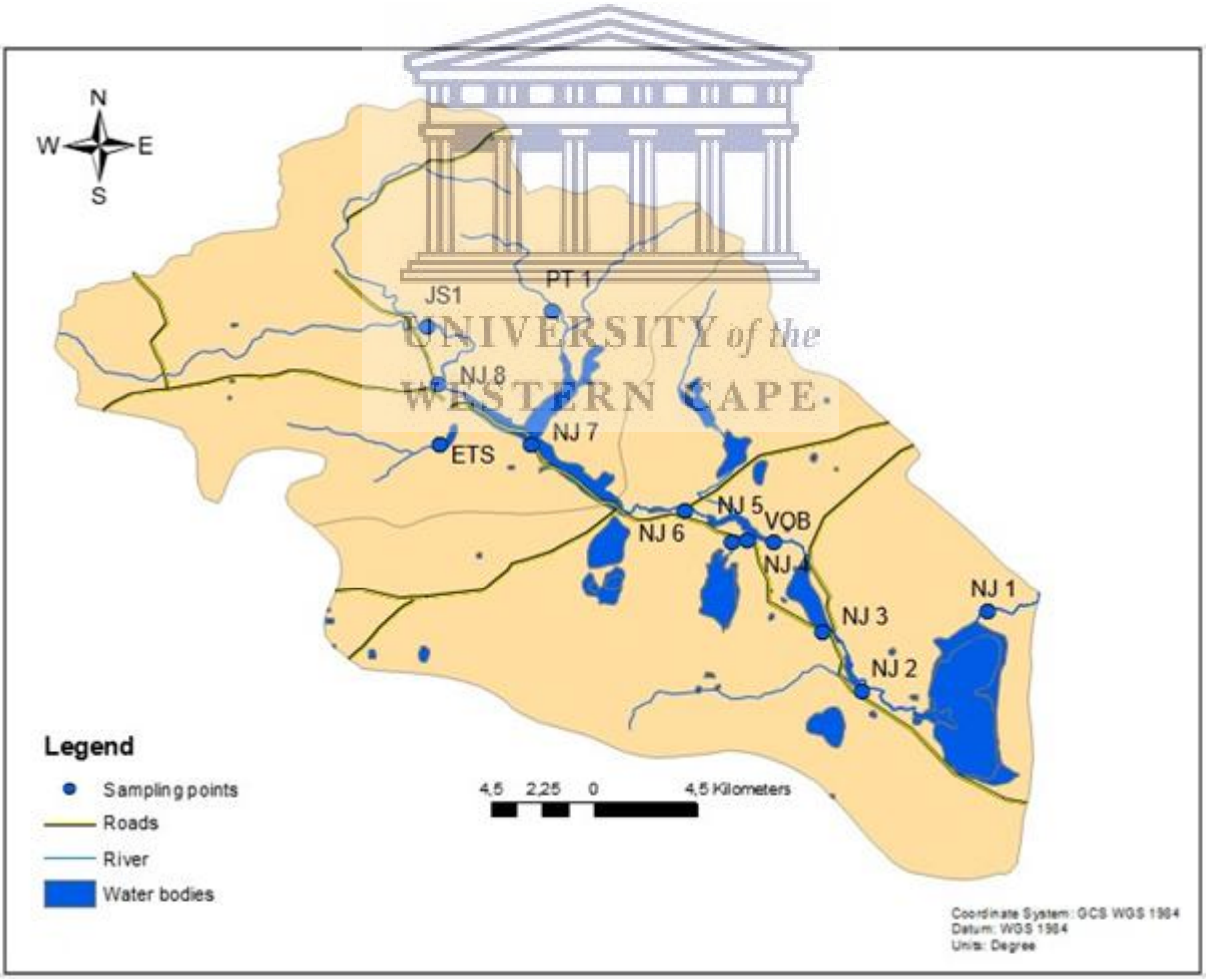


Figure 6: Location and distribution of surface water sampling points.

Table 2: Location and description of groundwater sampling points

Site Name	Description of location	Latitude	Longitude	Depth m
BH 1	Downstream at SANParks	-34.71587	19.93937	20
BH 2	Downstream west of Soetendalsvlei	-34.69419	19.96864	16
BH 3	Downstream east Soetendalsvlei	-34.72023	19.99792	40
BH 4	At Moddervlei	-34.60535	19.79761	50
BH 5	At Moddervlei	-34.60535	19.79758	20
BH 6	At Moddervlei	-34.60561	19.79758	50
BH 7	At Moddervlei	-34.60561	19.79753	20
BH 8	At Moddervlei	-34.60531	19.79741	8
BH 9	Upstream Near Spanjaardskloof	-34.52958	19.75255	60
BH 10	Upstream Near Spanjaardskloof	-34.52961	19.75252	20
BH 11	Near Boskloof	-34.53489	19.82909	60
BH12	Near Boskloof	-34.53485	19.8291	20
BH 13	Upstream west of Elim	-34.58694	19.66944	55
BH 14	Upstream west of Elim	-34.58694	19.66944	20
F1	Artesian borehole west of Elim	-34.58675	19.66547	-
F2	Artesian borehole west of Elim	-34.58575	19.66911	-
F3	Spring west of Elim	-34.58719	19.67817	-
F5	Upstream near Boskloof	-34.54494	19.8575	60
PZ 2	At Voelvlei	-34.68037	19.8699	7.3
PZ 8	Near Voelvlei	-34.64771	19.90303	10.6
PZ 14	Downstream near SANParks	-34.68683	19.92447	4
PZ 16	Downstream At SANParks	-34.71565	19.93941	9.3
PZ 19	Downstream north of Soetendalsvlei	-34.68792	19.99611	3.2
PZ 26	At Moddervlei	-34.60558	19.79747	3.4

BH =Borehole
PZ = Piezometer
F1& F2 = Artesian Borehole
F3 =Spring
F5 = Borehole upstream

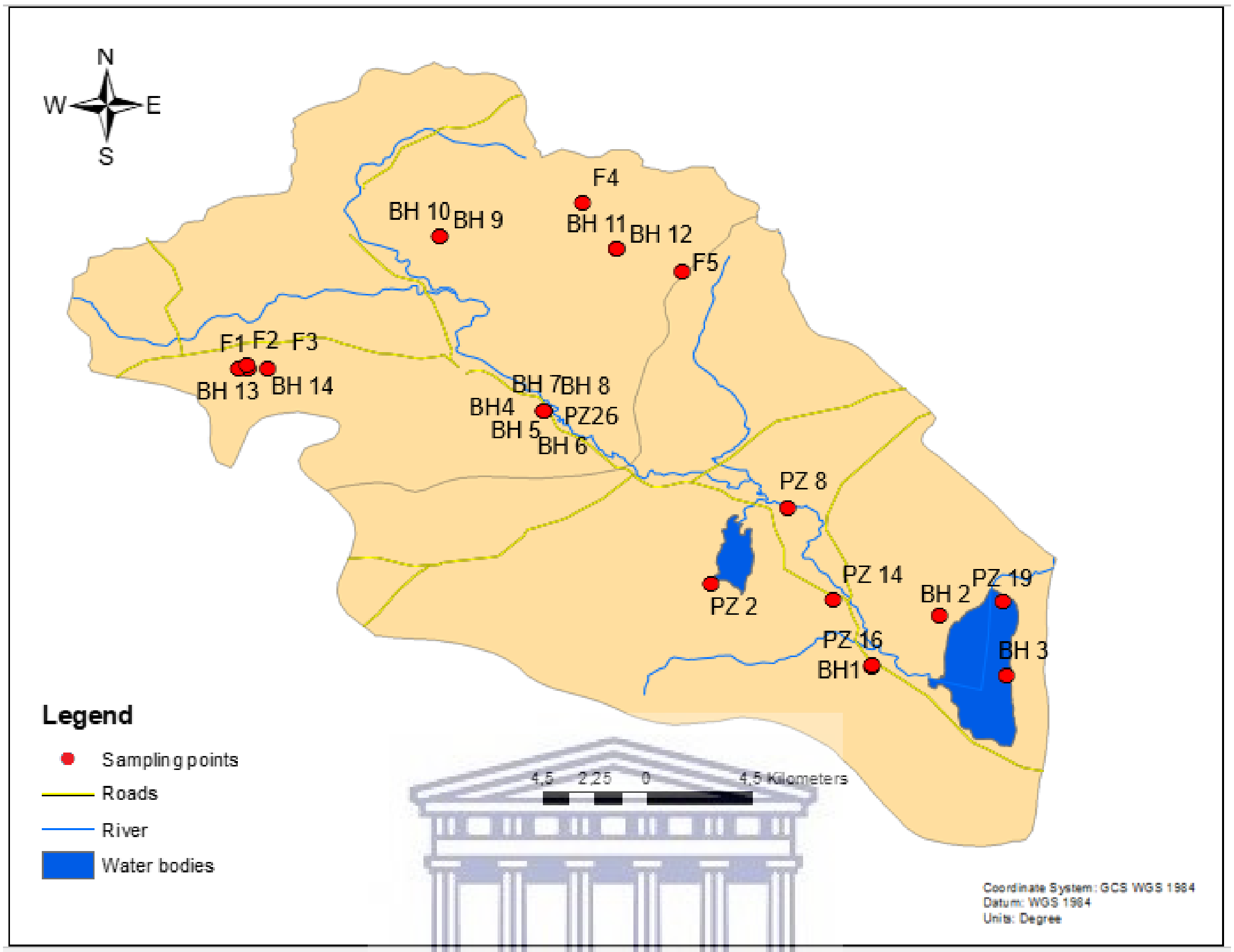


Figure 7: Location and distribution of groundwater sampling points.

Table 3: An indication of sites sampled during each sampling campaign.

Site name	July (2017)	October (2017)	March (2018)	July (2018)
	(Wet Season)	(Dry Season)	(Dry Season)	(Wet Season)
NJ 1	√	√	√	√
NJ 2	√	√	√	√
NJ 3	√	√	√	√
NJ 4	√	√	√	√
NJ 5	√	√	√	√
NJ 6	√	√	√	√
NJ 7	√	√	√	√
NJ 8	√	√	√	√
VOB	√	√	√	√
PT 1	√	√	√	√
JS1	X	√	√	√
ETS	X	X	√	√
BH1	√	√	√	√
BH 2	X	X	√	√
BH 3	√	X	√	√
BH 4	√	√	√	√
BH 5	√	√	√	√
BH 6	√	√	√	√
BH 7	√	√	√	√
BH 8	√	√	√	√
BH 9	√	√	√	√
BH 10	√	√	√	√
BH 11	√	√	√	√
BH 12	√	√	√	√
BH 13	√	√	√	√
BH 14	√	√	√	√
F1	√	√	√	√
F2	√	√	X	√
F3	√	√	√	√
F5	√	√	√	√
PZ 2	√	√	√	√
PZ 8	√	√	√	√
PZ 14	√	√	√	√
PZ 16	√	√	√	√
PZ 19	√	X	X	X
PZ 26	X	√	√	√
Sampled	√			
Not Sampled	X			

Borehole information

Boreholes presented in Figures 8 and 9, were drilled for the purpose of meeting the objectives of the Non-perennial Rivers project, the larger project that this study falls under. The depth and locations of these boreholes were carefully and specifically selected in order to meet a number of objectives set out by the project. These included the ability to evaluate the difference in hydraulic properties between different vertical levels (e.g. shallow and deep groundwater), conducting tracer and pumping tests to determine the influence of pumping on the hydraulics of the area. For this study in particular, the assessment of groundwater chemistry was done for the different formations and geological layers. The lithology of the constructed boreholes are presented in Figures 8 and 9.

Figure 8: Lithological cross section of boreholes upstream of the Nuwejaars Catchment.

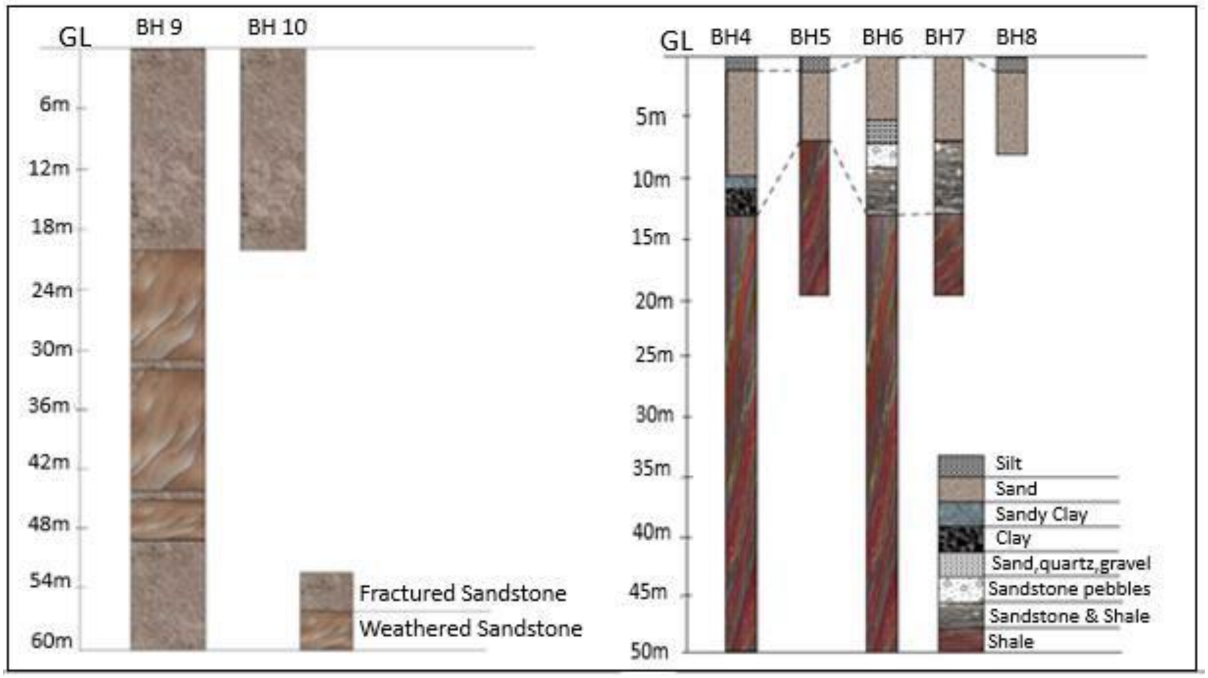


Figure 9 : **Lithological cross section of boreholes located at Spanjaarskloof and Moddervlei.**

Chapter 4: Research design and methods

4.1 Introduction

This chapter describes the research design and methodology applied to meet the objectives of this study. Data collection and analysis methods used to acquire, prepare and interpret water quality data are also described. This chapter provides a description of the quality control measures taken to ensure the validity of results, ethical considerations and the limitations encountered during this study.

4.2 Research design

The current study followed a quantitative approach, which provides the ability to explore relationships between variables, making it possible to characterize water chemistry. Four sampling campaigns were conducted in order to characterize the chemistry of surface water and groundwater during dry and wet seasons. Groundwater samples collected at depths below 10m from the surface were collected to represent deep groundwater, while samples collected from piezometers usually at depths less than a maximum of 5m from the surface were collected to represent shallow groundwater. Samples collected in July 2017 and July 2018 represented the onset of the wet season in each year, while those collected in October 2017 represented the beginning of the dry season and those collected in March 2018, the driest months of summer. Field parameters (temperature, electric conductivity, dissolved oxygen and pH) were measured while water samples were collected for hydrochemical and isotope analysis. Descriptive statistics were used to summarise large sets of data, while bivariate statistical analysis evaluated the strength of the relationship between variables. Furthermore, multivariate statistical methods were used to identify similarities between groups of samples based on their chemical compositions. Isotope signatures of deuterium and oxygen-18 were assessed to establish interactions between groundwater and surface water within the study area.

4.3 Data Collection

4.3.1 Field sampling

Surface water and groundwater were sampled between July 2017 and July 2018. Surface water samples were collected from selected sites along the river when it flowed. In the absence of flow, water samples were collected from pools that formed within the river channel. Water samples representative of deep groundwater were collected from boreholes, artesian boreholes, and springs, while subsurface or shallow groundwater was collected from piezometers. Borehole samples were collected at specific depths within the screen, using a specific depth sampler, while the static water level was measured using a Solinst water-level meter, prior to sampling. Piezometers were purged before sampling to remove the top column of stagnant water. Due to the dry conditions experienced in the area during the study, some piezometers became dry and were only sampled in July 2017 (see Table 3). The location and description of the sampling points are presented in Tables 1 and 2.

Samples for hydrochemical analysis were stored in 250 ml polypropylene plastic bottles, pre-cleaned with 10% hydrochloric acid and phosphate-free detergent from Kimix chemicals and thereafter rinsed with deionized water. Samples for analysis in the laboratory were filtered through a 0.45-μm Munktell filter, kept cool in the field using a cooler box and stored in a refrigerator at a temperature of 6°C until they could be analysed, within a few days after collection.

Isotope samples, including a rainfall sample were collected in 50ml plastic bottles, and filled completely to the top, avoiding any bubbles, before sealing. Isotope sampling bottles were tightly capped to avoid evaporation. Unlike those collected for nutrient and major ion analysis, these samples were not filtered. Although, if kept cool, isotope samples have a long shelf life, collected samples were analysed within 3 weeks after sampling.

4.3.2 Field measurements

A HACH HQ40d multi-meter was used to measure temperature, EC, pH and DO in the field. Total alkalinity was titrated in the field using indicator powder pillows, phenolphthalein and bromcresol green-methyl red; the titrant was a standard solution (0.020N) of sulphuric acid.

4.3.3 Laboratory analysis of water samples

Nutrients were analysed using a HACH DR 6000 UV/VIS Spectrophotometer and a HACH DR 200 reactor for digesting samples for analysis for total nitrogen and total phosphorus. Low- range methods were selected in order to ensure that detection limits would be suitable for samples with low concentrations. When measured concentrations were below the measuring range of the method, samples were recorded as below detection limit. Standards recommended by HACH were used for each of the analyses. Table 4 summarises the methods, detection limits, accuracy-check methods and standards used during the analysis of nutrients. The HACH Company claims precision at a 95% confidence interval.

Table 4: Analysis methods, detection limits and standards for accuracy checks, used during nutrient analysis.

Parameter	Method	Measuring range (mg/L)	Standard for accuracy check
Nitrate	Cadmium reduction Method	0.3 -30	Nitrate Nitrogen
Total Nitrogen	Persulfate Digestion Method	0.5 – 25	Ammonia Nitrogen
Total Phosphorus	PhosVer3 with Acid Persulfate Digestion	0.06 - 3.5	Phosphate standard solution
Phosphate	Molybdovanadate Method	0.3 – 45	Phosphate standard solution

Information available from: https://www.hach.com/

Major ions were analysed at the national Department of Agriculture laboratory in Elsenburg using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Analyses was performed using a high performance iCAP 7600 ICP-OES Radial Spectrometer, manufactured by Thermo Fisher Scientific. The detection limit and sensitivity of the instrument varies from element to element. Minimum detection limits provided for the instrument include calcium 0.02 µg/L, potassium 5.10 µg/L, magnesium 0.04 µg/L and Sodium 1.80 µg/L. (Information available on manufacturer's website: http://www.thermofisher.com).

Samples for stable isotopes were collected in March and July 2018. The analysis of stable isotopes was conducted in the Earth Sciences Department at the University of the Western Cape, Bellville, South Africa. For this analysis, the off-axis integrated cavity output spectroscopy (OA-ICOS) method was used. It was performed on a LGR DLT-100 liquid water isotope analyser (model 908-0008-2010) manufactured by Los Gatos Research Inc. (Mountain View, California, USA). The instrument was connected to a LC PAL liquid auto-sampler (model 908-0008-9001) manufactured by CTC Analytics, for the simultaneous measurement of $^{2}H/H$ and $^{18}O/^{16}O$ ratios of water samples. The auto-sampler was inserted with a SGE 5µl (model 5F-C/T-0.47/5C) syringe for the injection of water samples into a heated injector block (85°C). According to the manufacturer specifications (Los Gatos Research Inc.), the model of the isotope analyser provides a 1-sigma precision below 0.6‰ and 0.2‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively. (Information available on company website: www.Igrinc.com)

All values are expressed in the standard delta notation in per mill (‰) relative to VSMOW as:

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \qquad (4.1)$$

where, R is the ratio of the heavy to the light isotope (e.g. $^{18}O/^{16}O$) of the sample and the standard.

4.4 Data Analysis

Water quality data is characterized by missing values or gaps, values that fall above and below the detection limit, outliers and, usually, data that are not normally distributed (Solomon, 2013). Some of these characteristics are evident in the data collected during this study, particularly due to the extreme drought experienced during the sampling period.

Descriptive statistics (min, max, median, standard deviation) and correlation analyses were used to describe the nature of the data, as well as to describe relationships between variables. In correlation analysis, the strength of the relationship between two samples is indicated by the correlation coefficient (r). A strong positive or negative linear relationship between two variables is indicated by an r value near 1 or -1, while an r value approaching zero indicates little to no relationship between two variables (Solomon, 2013; Laar, 2018)

Statistical tests such as Independent t Tests and Repeated Measures ANOVA were conducted using the IBM® SPSS® Statistics 21 software to evaluate significant differences between groups of water quality data. Statistical tests were set to analyse data at a 0.05% level of significance. Independent t Tests were used to evaluate significant differences in water quality between the upper and lower regions of the catchment. Repeated Measures ANOVA which allows for the analysis of measurements taken over different time periods was conducted to test for significant temporal variations in water quality parameters. To meet the requirements for these tests, hydrochemical data was transformed using the Log 10 function in SPSS, to achieve a normally distributed dataset. Other assumptions required such as the homogeneity of variances and sphericity of the covariance matrix were tested during the procedure. In the event that requirements of one of these assumptions were not met, alternative corrected results provided by the software were reported instead. For example, when the assumption of the sphericity of the covariance matrix was violated, values produced by the Greenhouse-Geisser correction where reported. The Repeated Measures ANOVA test, did not allow for groups with different total numbers of samples (N) to be analysed. As a result, the assessment of temporal changes in water quality in this thesis excludes a few samples (2 surface water and 4 groundwater samples) that were not collected during all 4 sampling campaigns. However, the spatial assessment of water quality accounts for the entire data set.

The application of multi-variate statistics in water resources is widespread, especially in fields such as hydrogeology and hydrogeochemistry. These statistical methods are particularly useful when analysing a dataset containing multiple variables. This approach provides the ability to make comparisons or identify differences or similarities in samples, a tool useful in water chemistry (Solomon, 2013). In this study, Principle Component Analysis (PCA) and Cluster Analysis (CA) were conducted, using PRIMER version 6.1, a statistical package commonly used for community ecology and environmental science (Clarke and Gorley, 2006). The PCA and CA analyses included the majority of the parameters assessed during this study (temperature, pH, EC, total nitrogen, total phosphorus and major ions). Only nitrate and phosphate were not included in the analysis because their concentrations are also represented by total nitrogen and total phosphorus.

PCA identifies patterns in a data set, while CA allows for similar or dissimilar samples to be identified based on their chemical composition (Bhat et al., 2013; Solomon, 2013), a way of further classifying and characterizing water quality based on a combination of variables. Combined, these two methods minimise the number of dimensions in a data set and also prevent the possibility of losing valuable information (Laar, 2018). CA and PCA group similar samples into clusters or groups, hence the clustering of groundwater and surface water samples provides an indication of similarities between the two water sources.

Prior to conducting PCA and CA, data was first transformed using the log function as required, based on the distribution of the raw data. The data included in the analysis consisted of different units (mg/L, mS/m, °C), and the numerical spread of data generally varied from variable to variable, which is common with environmental data, therefore the data also required normalising. Normalising transforms data so that is has a mean of zero and a standard deviation of one, making all the variables comparable.

Cluster Analysis (CA) is a multi-variate statistical method that allows for the classification of variables or samples into groups based on a measure of their similarities (Bhat et al., 2013). The resemblance of samples was generated and represented by a resemblance matrix. In this study, Hierarchical Agglomerative Clustering Analysis was used to group samples based on their similarities or dissimilarities in terms of their chemical composition. CA produces a graphical representation called a dendrogram that exclusively group's similar samples into clusters, based on an assigned distance (Solomon, 2013). This study selected Euclideandistance as a measure of similarity and the complete linkage cluster mode for the generation of the dendrogram.

The Piper diagram allows for the evaluation of water type or hydrochemical facies, which gives an indication of the origin of water (Kumar, 2013). Piper diagrams proposed by (Piper, 1944) were generated using the Geochemist's Workbench student edition 12.0. These plots were generated from hydrochemical data of major ions, using the percentages of major ion abundances of samples in meq/L. Water type on these plots is determined by the position of the water sample on the Diamond. This position is based on where each sample plots on the two ternary diagrams that represent the ionic proportions of cations on one triangle and that of anions on the other (Kumar, 2013).Waters that plot within the same region are of the same type and are therefore likely to originate from the same source.

To identify and assess changes in water quality during the wet and dry season, box plots showing concentrations of each variable for each sampling campaign were generated using XLSTAT, a statistical extension of Microsoft Excel. On the other hand, to assess spatial differences in variables across the catchment, spatial distribution maps were generated using Arc Gis software version 10.4.1. Shapefiles used for the generation of these maps were acquired from NGI (National Geo-spatial Information) and from the Water Resources of South Africa (WR2012).

Isotope compositions, expressed in per mil (‰) deviations from the VSMOW standard of δ^2H and δ^{18}O, were plotted on a δ^{18}O vs δ^2H plot for interpretation. Precipitation data acquired from (Harris et al., 2010) was used for the generation of the local meteoric water line (LMWL). In addition, the global meteoric water line (GMWL) defined by (Craig, 1961), which provides a reference for interpreting the provenance of groundwater, was plotted on the δ^2H vs δ^{18}O plot based on the following equation;

$$\delta^2H = 8 \times \delta^{18}O + 10 \text{ ‰ VSMOW} \qquad (4.2)$$

4.5 Reliability and validity of results

To ensure the accuracy and reliability of the results obtained during data collection and analysis, a variety of quality control measures were undertaken. Prior to each field visit, field instruments were calibrated as recommended in the relevant User Manuals. Standard sampling methods were used and blank samples consisting of distilled water were used as controls.

The HACH DR 6000 UV/VIS spectrophotometer used for nutrient analyses provides integrated quality assurance software that improves the accuracy of the results. Furthermore, an accuracy check using the standard solution method was conducted for each test to validate the accuracy of the test procedure, the reagents and the lab instrument. This accuracy test gave the option of adjusting the calibration, which reduces inaccuracies, and allowed for a 95% confidence interval of precision to be achieved. During laboratory analysis, blanks were used to zero or clear the spectrophotometer before taking actual readings to minimise errors. Similarly, during the analysis of major ions, the spectrometer was calibrated before analysis and a quality control test was conducted. The quality control procedure was conducted after analysing every 12 samples and was set at a 10% limit to warn for failure or any inaccuracies.

Prior to data analysis, the accuracy of the hydrochemical analysis of major ions was validated using the cation-anion balance (CAB). In theory, all portable waters are electrically neutral, hence it is expected that the sum of cation and the sum of anions in a sample must balance or be equal. This is known as the principle of electroneutrality, which governs the reliability of the hydrochemical analysis conducted on major ions (Younger, 2007). The cation-anion balance was calculated using Equation 4.3;

$$\mathrm{CAB\%} = 100 \times \frac{\text{sum of cation concentrations} - \text{sum of anion concentrations}}{\text{Sum of cation + anion concentrations}} \tag{4.3}$$

According to Younger (2007), the results of water samples that yield a CAB, below ±5% can be regarded as accurate and suitable for all uses, while those that yield a CAB between ±5 and ±15% should be used with caution. The results obtained from water samples that yield a CAB above ±15% cannot be regarded as accurate and should therefore not be used for serious decision-making or scientific use. The CAB computed for samples collected during the study period are presented in Table 6.

The isotope analyser, according to the manufacturer specifications (Los Gatos Research Inc.) provides a 1-sigma precision below 0.6‰ for δ^2H and 0.2‰ for δ^{18}O. Furthermore, standard maintenance of the instrument was performed prior to analysis, which includes cleaning the transfer line and injector block and changing the injection-port septum. Deionised water was used for the cleaning and priming of the syringe at the beginning and end of each test run. The procedure made use of LIMS (Laboratory Information Management System) for Lasers 2015 (version 10.096), which assists in data corrections, graphical evaluation of sample injections for water yield variation, between-sample carryover corrections, instrumental drift and nonlinearity, and data normalization. (Wassenaar et. al., 2014). For improved accuracy, the reported value is based on the average of 6 injections.

4.6 Research integrity

Permission to sample on private property was requested, prior to conducting field visits. No other activities undertaken during this study required ethical considerations.

4.7 Study limitations

- A lack of comprehensive chemical records for the study area did not allow for natural or reference conditions of water quality to be set.
- A number of piezometers drilled for research purposes by the University of the Western Cape prior to conducting the current study were damaged. This limited the number of sampling points available for the study.
- Due to the nature of N-PRs, river samples could not always be collected from a flowing river, especially during dry months that experienced zero flow. Instead, where possible surface water samples were collected from pools within the river channel. Gaps in the data set therefore exist.
- An inadequate number of rainfall collectors within the catchment, limited the number of rainfall samples that could be collected for isotope analysis.

Chapter 5: Results and Discussion

5.1 Introduction

This chapter reports on findings regarding the physico-chemical and environmental isotope compositions of groundwater and surface water in the Nuwejaars Catchment, collected between July 2017 and July 2018. In sections to follow, water chemistry in the Nuwejaars Catchment is characterized by assessing, seasonal and spatial differences in chemical compositions of groundwater and surface water and by, identifying hydrogeochemical processes that influence groundwater chemistry. Results obtained from isotope analysis are also discussed and interpreted to establish interactions between groundwater and surface water within the study area. Key results obtained for each objective are described, interpreted and compared to findings reported on by previous studies. For the purpose of interpretation in this chapter, deep groundwater refers to groundwater collected from boreholes at sampling depths greater than 10m from the surface, while shallow groundwater refers to groundwater collected nearer to the surface from piezometers, at depths not more than 5m from the surface. The term groundwater refers to both deep and shallow groundwater sources.

5.2 Characterization of major constitutes of water

Physical and chemical properties of water resources in the Nuwejaars Catchment are presented in Table 5. Measures of variability (min, max and standard deviations) and measures of central tendency (mean) have been used to summarise and describe the variability and distribution of the results obtained. The information below, provides a statistical summary of the data, detailed results are presented in Appendix 1. The results obtained from the Independent t Tests and Repeated Measures ANOVA significance tests are presented in Appendix 7.

Table 5: Statistical summary of physical and chemical properties of water resources in the Nuwejaars Catchment, July 2017-July 2018.

		Surface water n= 10				Deep groundwater n= 15			
Parameter	**Sampling month**	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Temp °C	July (2017)	12.2	19.7	15.9	2.4	14.3	19.7	17.3	1.6
	October (2017)	16.4	24.5	20.0	2.3	17.2	21.1	19.0	1.5
	March (2018)	22.1	26.0	23.9	1.2	18.5	23.2	20.6	1.1
	July (2018)	12.1	19.3	15.9	2.0	16.8	22.8	18.6	1.7
pH	July (2017)	6.4	8.4	7.4	0.7	5.3	8.2	6.7	1.0
	October (2017)	6.2	7.9	7.2	0.6	4.9	7.4	6.4	0.8
	March (2018)	6.1	8.8	7.7	0.8	5.0	8.9	6.3	1.0
	July (2018)	5.7	8.1	7.1	0.8	4.4	7.5	6.0	1.1
	July (2017)	4.7	12.8	8.1	2.7	2.4	9.9	5.3	2.1
	October (2017)	3.8	9.5	7.7	1.8	1.9	9.3	3.8	2.0

DO (mg/L)	March (2018)	4.0	11.9	7.5	2.3	1.8	10.2	3.6	1.9
	July (2018)	3.3	8.6	6.2	1.6	1.0	4.3	2.0	1.0
EC mS/m	July (2017)	54.8	3740.0	841.1	1112.0	32.0	1398.0	396.3	512.9
	October (2017)	56.1	998.0	177.8	289.2	0.6	1329.0	344.8	475.2
	March (2018)	64.6	2590.0	828.0	915.8	33.6	2990.0	631.5	963.6
	July (2018)	45.2	2744.4	805.9	1020.5	20.8	2084.2	474.3	696.3

b) Shallow groundwater n= 5

Parameter	Sampling month	Min	Max	Mean	SD
Temp °C	July (2017)	14.5	18.9	17.2	1.6
	October (2017)	17.5	19.6	18.7	1.0
	March (2018)	20.3	22.4	21.4	0.8
	July (2018)	14.9	19.3	17.6	1.8
pH	July (2017)	6.6	7.4	7.1	0.4
	October (2017)	6.5	7.2	6.8	0.3
	March (2018)	6.8	7.3	7.0	0.2
	July (2018)	6.6	7.1	6.8	0.3
DO mg/L	July (2017)	2.5	4.5	3.4	0.7
	October (2017)	2.6	5.7	4.1	1.1
	March (2018)	1.1	4.2	3.1	1.2
	July (2018)	1.6	5.0	2.5	1.4
EC mS/m	July (2017)	3510.0	5730.0	4674.0	1079.1
	October (2017)	2760.0	6460.0	4532.0	1668.0
	March (2018)	3100.0	6620.0	4972.0	1683.3
	July (2018)	2379.1	4430.9	3545.9	1017.2

5.2.1 Water temperature

Temperature values, recorded for surface water and groundwater during the sampling period are presented in Table 5. Strong seasonal variations in surface water temperature in the Nuwejaars Catchment were observed during the sampling period (F (3, 27) = 68.13, p= <0.001). These variations can be primarily attributed to the time of sampling and effects of seasonality. Surface water temperature ranged between 12.1°C and 26°C during the duration of the investigation. The lowest surface water temperatures were recorded during the winter sampling periods of July 2017 and July 2018 with mean values of 15.9 °C. The highest surface water temperature values were recorded during the onset of the dry season in October 2017 and dry season of March 2018, with mean values of 20°C and 23.9° C, respectively. A mean difference of 8°C between the lowest and highest mean values recorded during the sampling period, was observed in surface water temperatures. Temperature differences recorded for surface water during summer and winter were expected since surface water bodies are in direct contact with air temperatures.

Surface water temperatures in the upper and lower sections of the catchment did not vary significantly during all 4 sampling campaigns (p-values = 0.66, 0.21, 0.29 and 0.13). However, water temperatures were observed to be slightly lower upstream. This slight difference in water temperatures can be attributed to differences in elevation. Water temperatures upstream at higher elevations are expected to be lower because temperature generally decreases with an increase in elevation.

A gradual increase in deep groundwater temperatures was observed during the beginning of the sampling period in July 2017 to March 2018, after which temperatures dropped during the winter season of 2018. Temporal variations in deep groundwater temperatures during the duration of the study were therefore observed (F (3, 42) =23.60, p = <0.001). Deep groundwater temperatures ranged between 14.3°C and 23.2°C during the sampling period. The highest temperatures were also recorded in the dry season of March 2018 with an average value of 20.5°C, while the lowest deep groundwater temperatures were recorded during winter in July 2017 with a mean of 17.3°C. This pattern was observed because groundwater that is approximately 5-150m below the surface tends to be related to the mean annual air temperatures (Younger, 2007). Seasonal differences in deep groundwater temperatures were not as pronounced as compared to those observed in surface water. The mean difference between the lowest and highest water temperature recorded computed to 3.3°C. In general, groundwater temperatures do not normally fluctuate, they normally maintain a constant pattern, primarily because weather conditions on the surface do not influence groundwater temperatures to a large extent.

No significant differences in deep groundwater temperatures were recorded between the upper and lower sections of the catchment during July 2017 (p value = 0.06) and March 2018 (p- value = 0.9), however significant differences in deep groundwater temperatures between the two regions were observed during October 2017 (p value = 0.01) and July 2018 (p value = 0.03). Temperatures in deep groundwater upstream, usually above 18°C were observed, while groundwater temperatures below this value were recorded for the majority of boreholes across the rest of the catchment.

Shallow groundwater exhibited similar temperatures to those recorded for deep groundwater, although it is generally expected that groundwater in the shallow zone, which is affected by changes in temperatures on the surface to a larger extent, would yield temperatures similar to those of surface water. The highest and lowest mean values recorded were 17.2°C and 21.4°C in the wet and dry season respectively.

5.2.2 pH

pH values, recorded for surface water and groundwater during the sampling period are presented in Table 5. The minimum and maximum pH values recorded during the sampling period in surface water ranged from 5.7 to 8.8. Surface water pH was mostly between 7 and 8 and did not change significantly throughout the sampling period (F (2, 17) = 1.7, p = 0.22). According to Dallas and Day (2004), the pH of natural waters is expected to be close to neutral, ranging between 6 and 8. However, pH values below 6 were recorded, especially In July 2018 in tributaries of the Nuwejaars River (See Appendix 1). Spatially, surface water pH varied in the uplands and lower sections of the catchment for the majority of the sampling period (p values = 0.04) with the exception of pH values recorded during October 2017 (p value = 0.83). Lower pH values, below 6 were detected upstream and increased towards the coast.

According to Bickerton (1984), as observed by the current study, streams in the high lying mountainous parts of the catchment are acidic and become more alkaline in the low lying regions of the catchment. Lower pH values detected upstream of the catchment, can be attributed to the presence of leachates from fynbos vegetation (Raubenheimer and Day, 1991).The presence of fynbos causes the process of acidification to occur, promoting the production of hydrogen ions, thus lowering pH in waters (DWAF, 1996). Furthermore, the slightly acidic nature of surface waters in the uplands the catchment is due to the quartzitic Table Mountain Group (TMG) over which these rivers flow (Mazvimavi, 2017). Surface water pH nearer to the coast was either approaching or slightly above 8. According to Hinga (2002) and Laar (2018), the pH of coastal waters is generally close to 8.2, however the alkaline nature of waters can also be attributed to the calcareous nature of the southern Agulhas plain. The presence of more alkaline waters downstream can also be attributed to photosynthetic processes that occur as the river flows through the floodplain of the river.

Spatial patterns observed by the current study for pH in surface waters of the Nuwejaars Catchment are consistent with those previously reported on in literature (Bickerton, 1984; Kraaij et al., 2009; Mazvimavi, 2017). In particular, Mazvimavi (2017) observed lower pH values (5- 6.5) during the months of August and September 2015, when most of the rainfall for 2015 was received, similarly, the lowest pH values of surface water during the current study were recorded in July 2018 (wet season).

A gradual decrease in the mean values of pH in groundwater can be observed from season to season (Figure 10b). Although groundwater pH values were generally below 7, pH in deep groundwater varied from season to season during the sampling period (F (3, 42) = 13.43, p= <

0.001). The lowest and highest mean ranged from 6 to 6.7 in July 2018 and July 2017 respectively (See Figure 10b). Deep groundwater pH recorded in the uplands and lower regions of the catchment varied during all 4 sampling campaigns (p value computed for July 2017 = 0.01, while October 2017, March and July 2018 computed p values < 0.001). Deep groundwater upstream yielded pH values well below 7, even as low as below 5 in artesian boreholes. Piezometric waters and boreholes in the mid sections and lower reaches of the catchment yielded the highest pH values, indicative of near neutral or slightly alkaline waters. These values were either approaching a pH of 7, or between a pH of 7 and 8.

The results indicate that the chemical composition of the underlying geology in different sections of the catchment largely influences the pH of groundwater. Upstream, pH values below 6 were measured due to the nature of the underlying Table Mountain Group (TMG) in the uplands of the catchment. The presence of carbonate bearing formations in the lower sections of the catchment, allows for rapid reaction rates of carbonate minerals, resulting in acid neutralisation and therefore more alkaline groundwater. Wu (2008) reported on pH values within regions of the TMG to range between 4.7 and 6.2, these findings can be confirmed by values obtained during the current study.

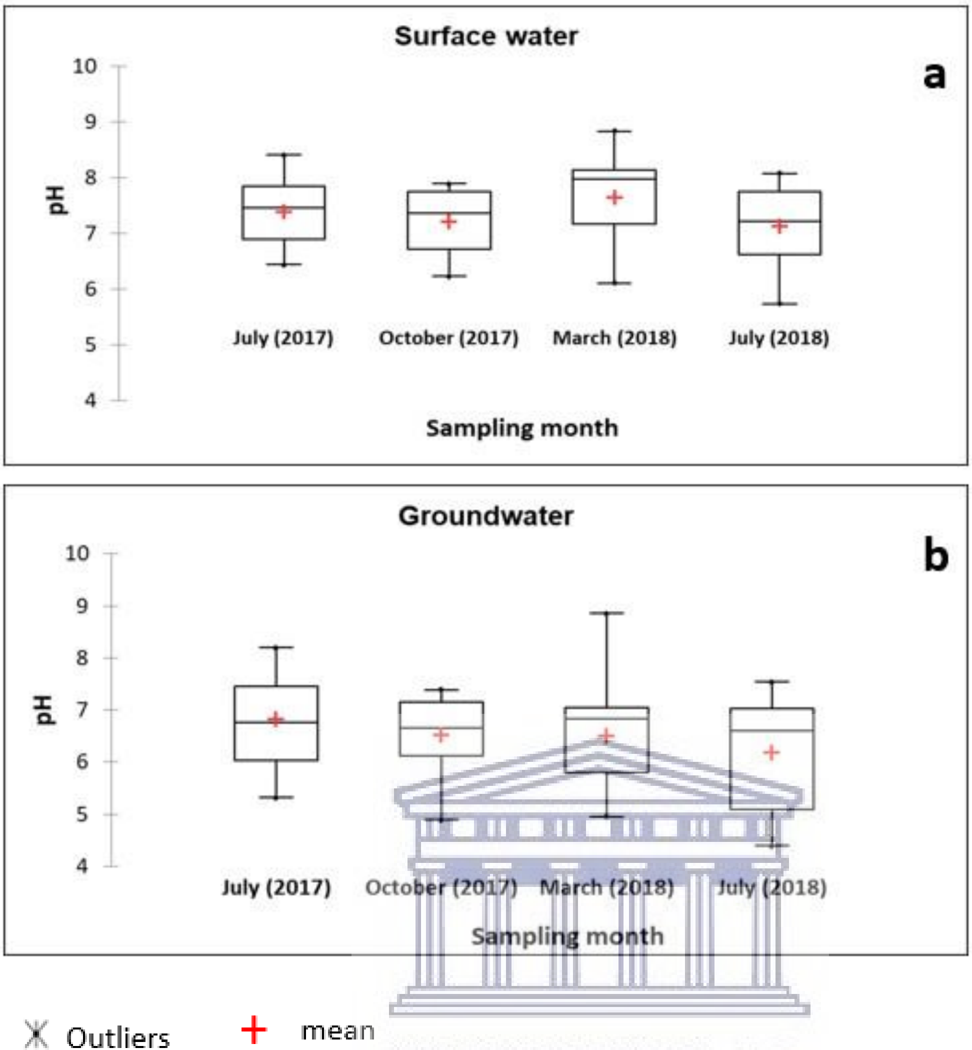


Figure 10: pH values of surface water (n= 10) and groundwater (n=20) during July 2017-July 2018.

5.2.3 Dissolved oxygen

Dissolved oxygen (DO) concentrations recorded during the study period are presented in Table 5. Dissolved oxygen in surface water ranged between 3.3 and 12.8 mg/L, while groundwater recorded lower values between 1 and 10.2 mg/L. This was expected because unlike surface water, groundwater is not directly exposed to the atmosphere and would therefore be characterised by lower oxygen levels (Rose and Long, 1988). Temporal variations in DO concentrations in both deep groundwater (F (3, 33) = 24.3, p = <0.001) and surface water (F (3, 24) =5.04, p = 0.008) were observed. Concentrations of DO for deep groundwater were generally below 5 mg/L, although a value above 10 mg/L was recorded during March 2018. DO concentrations in deep groundwater in the uplands and lower regions of the catchment did not vary significantly during July 2017 to July 2018 (p values = 0.49, 0.23, 0.57 and 0.67). The highest and lowest DO concentrations for both surface water and deep groundwater were recorded during July

2017 and July 2018 respectively. Ordinarily, DO concentrations are expected to be higher during winter months, when temperatures are cooler. This is because, DO generally increases with a decrease in temperature (Dallas and Day, 2004). The detection of lower DO concentrations during the winter period of July 2018 which is not expected can possibly be attributed to factors other than temperature such as, the decomposition of organic material or changes in photosynthesis rates by plants that also influence the amount of DO present in waters. In addition, the time of day at which DO reading are taken also largely influences the recorded values. Ideally, to avoid any inaccuracies, DO concentrations at a particular site should always be taken at the same time of the day to ensure accurate comparisons can be made over time.

DO concentrations in surface waters in the upper and lower regions of the Nuwejaars Catchment did not vary significant during the 4 sampling campaigns (p values = 0.13, 0.16, 0.31, 0.94). However, in some cases DO concentrations of values above 8 mg/L, were recorded in the uplands of the catchment, while DO concentration below 5 mg/L were recorded in the middle sections of the catchment. Lower DO concentrations in the lower topographical regions of the catchment are caused by the decrease in flow velocity from the high lying to low lying sections of the catchment, as a result of changes in the surface topography (Mazvimavi, 2017). DO concentrations above 8 mg/L recorded in the uplands of the catchment can also be attributed to influences of atmospheric pressure at higher altitudes (Dallas and Day, 2004). Also, temperatures are generally lower at higher elevations, and would result in increased DO concentrations in the recharge area of the catchment. DO readings downstream, particularly at NJ2, which recorded values as high as 12.8 mg/L can be due to the photosynthesis of riparian vegetation. Photosynthesis by plants causes an increase in DO concentrations (Dallas and Day, 2004). Spatial variations observed in DO concentrations of surface waters in the Nuwejaars Catchment are consistent with those recoded during 2014 and 2015 by Mazvimavi (2017).

5.2.4 Electric Conductivity (EC)

Electric conductivity (EC) values, recorded for surface water and groundwater during the sampling period are recorded in Table 5. Average EC values, from season to season, from highest to lowest were recorded as, July 2017 > March 2018 > July 2018 > October 2017. Seasonal variations and fluctuations in surface water EC were observed during the study period (F (3, 27) = 7.9, p value = 0.001), particularly downstream. Mazvimavi (2017) also reported on fluctuating EC values in surface water from season to season, with no real trend during 2014 and 2015, within the study area. EC in surface water was variable, ranging between a minimum of 45.2 mS/m and a maximum of 3740 mS/m, during the duration of the study.

In October 2017, EC values well below 100 mS/m were recorded upstream. At the beginning of the dry season in October 2017, minimal differences in EC were observed between the lower and upper regions of the catchment (t (9) = 1.56, p value = 0.15), with only NJ1 showing elevated concentrations (998 mS/m) as compared to the rest of the sampling sites. The October 2017 sampling campaign which marked the beginning of the dry season after the rainfall season, also recorded the lowest EC values, with a mean of 177 mS/m, for surface water during the sampling period. This can be attributed to the dilution of dissolved solutes during the rainfall season prior to sampling.

EC values recorded in deep groundwater varied between 0.6 and 2990 mS/m. Deep groundwater in the upper and lower regions of the catchment exhibited significant differences in EC values during the duration of the study (p values < 0.001). Deep groundwater from Boreholes and artesian boreholes located upstream of the catchment was fresh and yielded some of the lowest EC values recorded, usually with an EC value below 50 mS/m. Boreholes BH 1, 2 and 3, which are at the downstream end of the catchment, exhibited particularly elevated concentrations, generally, recording values higher than 2000 mS/m, and well exceeding this value on occasion. No significant temporal variations in the EC values of deep groundwater were observed (F (1, 16) = 3.1, p value = 0.09). The highest mean value (631 mS/m) for deep groundwater was recorded during the very dry period experienced in March 2018, while the lowest mean (344 mS/m) was recorded in October 2017, as was the case for surface waters.

Piezometric waters recorded the highest EC values during the duration of the study, ranging between a minimum and maximum of 2386 and 6620 mS/m. These values can be observed as outliers on Figure 11. The results indicate that shallow groundwater within the study area is more mineralized as compared to deep groundwater with EC values usually ranging between 4000 and 5000 mS/m (Figure 11). Higher EC values are usually expected in deep groundwater as compared to shallow groundwater, due to longer residence time in deeper groundwater systems, which favour the process of mineralization in groundwater (Hamutoko et al., 2017). However, the close proximity between the coast and the location of the piezometers and the presence of clay layers downstream, where the majority of the piezometers are located may influence the salinity of these waters. Clay soils are characterised by small particle sizes that bond together tightly, limiting the flow of water. This allows for more solutes to cling to soil particles within the subsurface, ultimately possibly influencing the water chemistry of shallow groundwater.

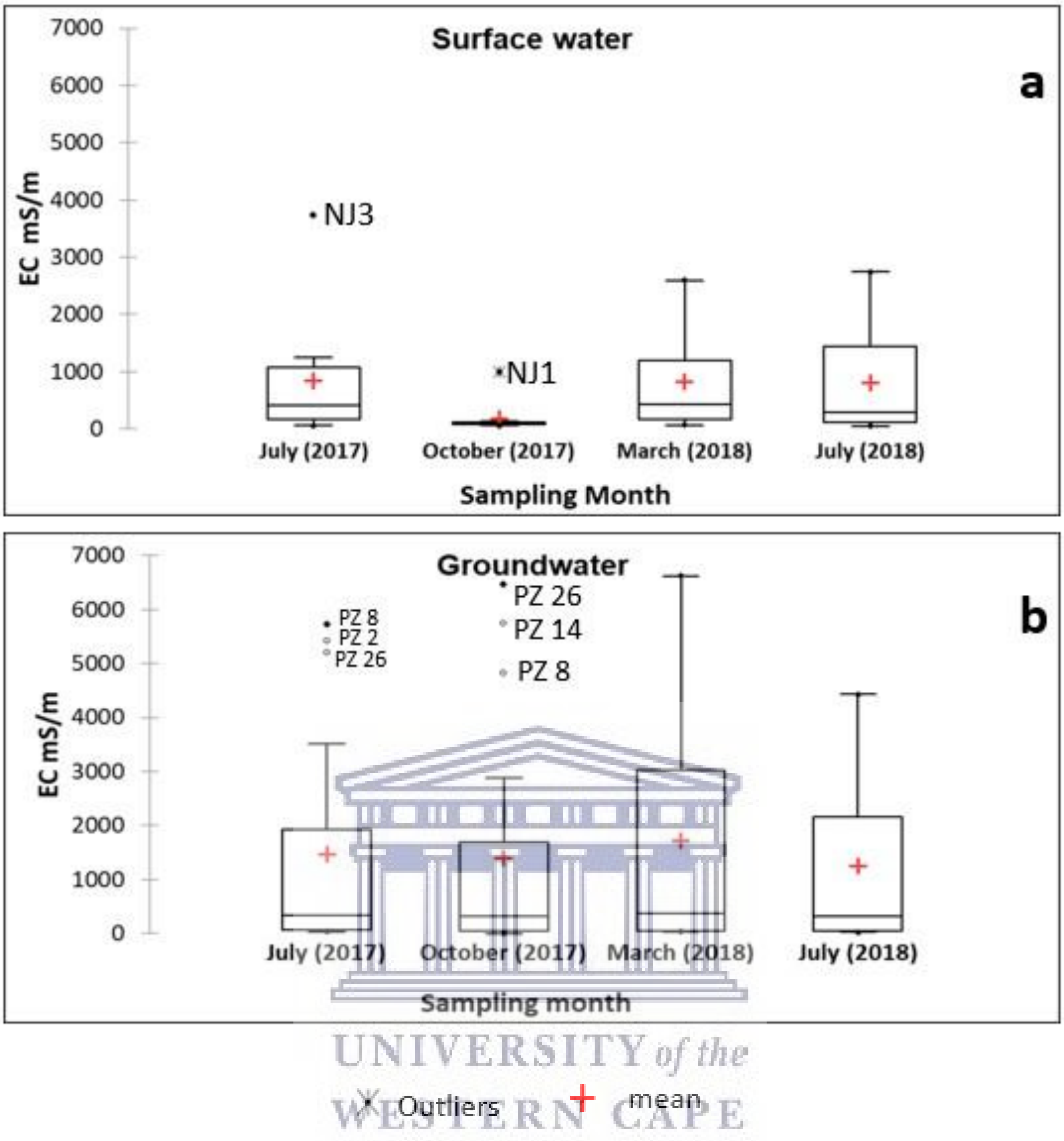


Figure 11: EC values of surface water (n=10) and groundwater during (n=20) July 2017- July 2018.

Average EC values of surface water across the catchment are presented in Figure 12. Variable EC values along the river were observed. Surface water EC in the upper and lower sections of the catchment did not vary considerably during 2017 (p values = 0.19 and 0.15), however significant differences in EC values between the two regions were observed during the dry and wet season of 2018 (p values = 0.01). Downstream river sites NJ1, NJ2 and NJ3 recorded the highest EC values, usually well above 1000 mS/m, primarily because solutes generally tend to accumulate downstream. This is because, while water travels downstream, natural processes and human activities continuously add inorganic salts to the system at a rate greater than their removal, by means of chemical precipitation or natural processes (DWAF, 1996). Changes in surface topography, reduce the velocity of flows at lower elevations, allowing for more accumulation of solutes downstream. Increased EC values downstream can also be attributed to evaporation from irrigated lands and the saline pans and lakes that the river flows through e.g Voelvlei and Soetendalsvlei (Mazvimavi, 2017). Furthermore, the Bokkerveld Group over which the river flows is also largely responsible for the saline nature of surface water downstream. Sea sprays also increase the salinity of river waters nearer to the coast.

River site NJ3, located downstream at a cattle farm, exhibited the highest EC concentrations recorded for surface water in July 2017 and July 2018. EC values at this site were up to 3740 mS/m, the highest recorded for surface water during the study period. EC concentrations recorded at NJ3, above 1000 mS/m can potentially be attributed to contaminants from the cattle farm entering the river, especially during the wet season. Surface water EC was generally lower upstream as seen on Figure 12. This is because, the upper section of the catchment is underlain by the TMG sandstones that are weathered, and in addition, the uplands of the catchment are primarily still in their natural state, therefore human activities do not affect water quality in this region. On the other hand, the middle and lower sections of the catchment characterised by higher EC values, consist of cultivated lands on and near the floodplain of the river. Cultivated areas are known to generate return flows that contribute to increased EC values (DWAF, 1996).

In N-PRs, the stagnation of river flows along certain reaches of the river can largely influence the EC value recorded at those particular sites. For instance, although minimal changes and lower EC concentrations were generally detected in the upper and mid sections of the catchment, river site NJ8, exhibited fluctuations in EC values over time. The Nuwejaars River at NJ8 was not flowing at the time of sampling during the dry season, hence samples were collected from a pool. Unlike flowing rivers, pools are characterised by stagnant water, more susceptible to abrupt chemical changes (Larned et al., 2010). These chemical changes are primarily driven be the process of evaporation. Changes in temperatures from season to season, that influence the rate of evaporation and the availability of water within the system are ultimately responsible for the variation in the water chemistry of pools. Although site NJ8 is also located near the town of Elim, where cattle have previously been seen grazing nearby, fluctuations in EC at this site can be attributed to the effects of evaporation. Water bodies that are not connected to the natural drainage system are characterised by high EC values due to the process of evaporation. Samples collected from JS1 (a tributary of the Nuwejaars River) were also collected from a pool, however, the EC values recorded at this site were particularly low. Information acquired from (Mazvimavi, 2017) suggests that tributaries of the Nuwejaars River are fed by fresh deep groundwater provided by springs. These pools upstream of the catchment form as a result of deep groundwater discharging to the surface.

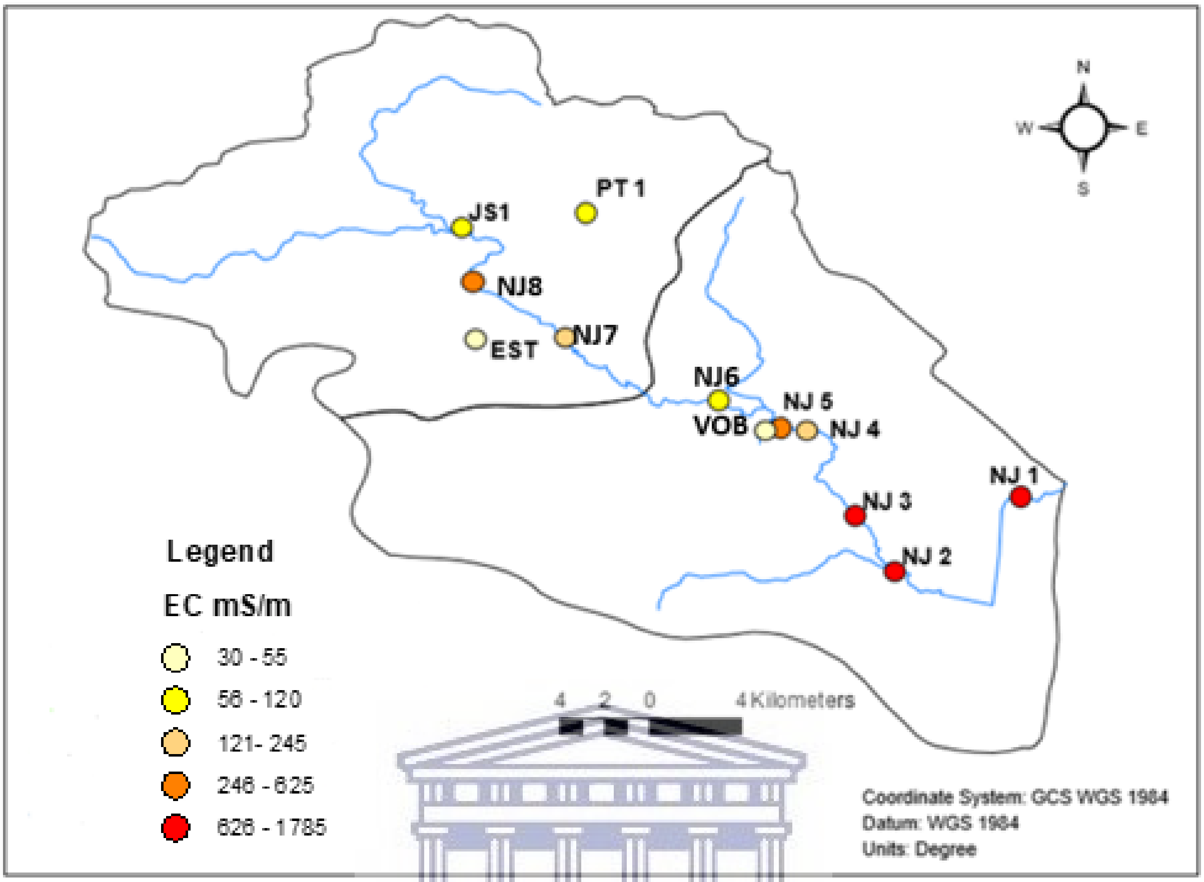
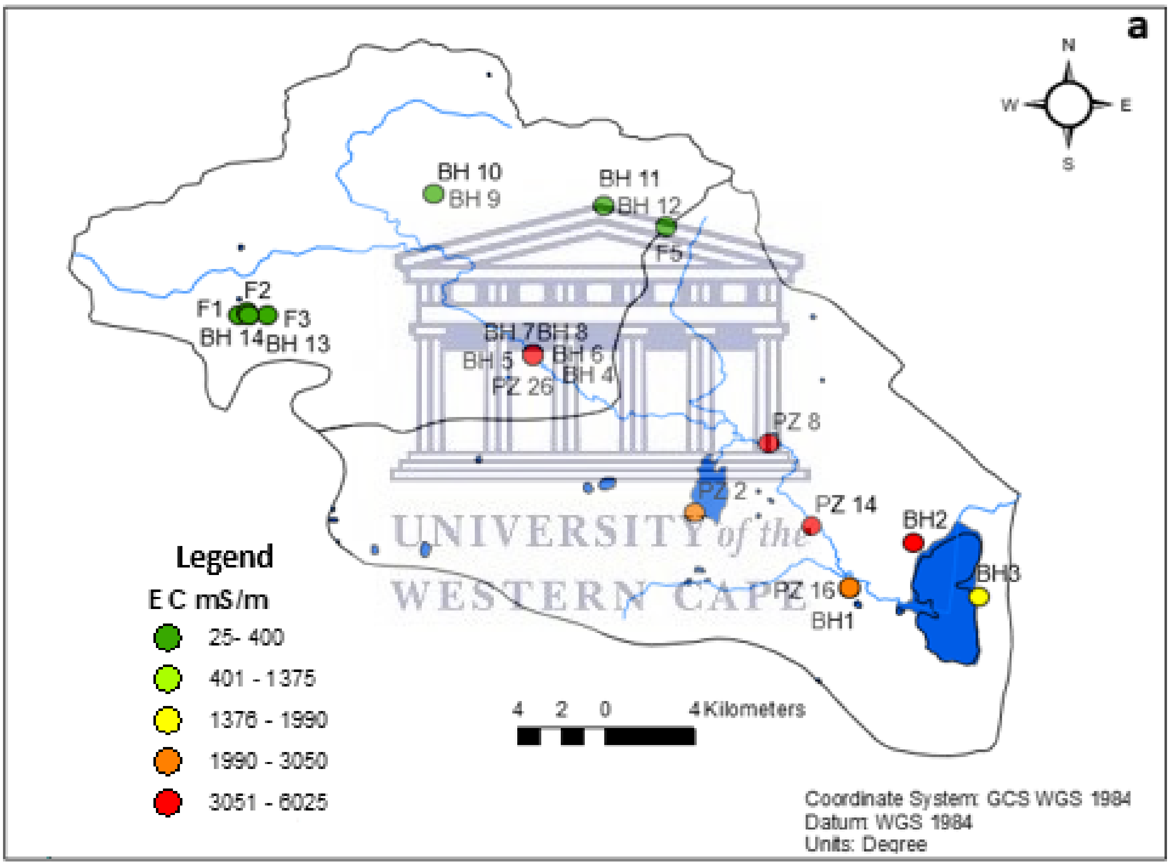


Figure 12: Spatial distribution of average EC values in surface water, July 2017 – July 2018.

Spatial variations of EC values in groundwater are presented in Figure 13. The groundwater spatial distribution map, shows an increase in EC concentrations downstream from the high-lying fresh recharge areas of the catchment to the lower-lying sections of the catchment near the coast. An increase in groundwater EC at the point of transition from sandstone into shale and then limestone can be observed, this indicates a strong association between groundwater EC and geology type within the catchment. According to Kinoti (2018), the Bokkeveld shale present in the mid sections of the catchment, is characterised by brackish to saline waters.

Fresh deep groundwater (EC <100 mS/m) in the upper Table Mountain Group (TMG) regions of the catchment, can be attributed to the weathered and fractured sandstone formations that underlie this area. These rocks are inert and therefore do not largely contribute to salinity. The upper sections of the catchment are also recharge areas, therefore more dilution is expected to occur in this region (Wu, 2008). The presence of fresh groundwater provides evidence of pronounced infiltration of rainfall as recharge into the aquifer. The EC values recorded for deep groundwater in the TMG regions of the study correspond with those reported on by Wu (2008), which indicate the presence of high quality, fresh groundwater in TMG regions.

Due to topographical changes, groundwater upstream flows faster, reducing contact time with aquifer material. On the contrary, due to low elevations, as low as 5m, almost at sea level, a small hydraulic gradient exists in the lower sections of the catchment. This limits groundwater flow resulting in groundwater with a long residence time, allowing longer contact periods between groundwater and the aquifer material. As a result, high EC concentrations were measured in the lower sections of the catchment. The results therefore indicate that groundwater EC in the Nuwejaars Catchment is influenced by geology type, infiltration rates and rock-water interactions.



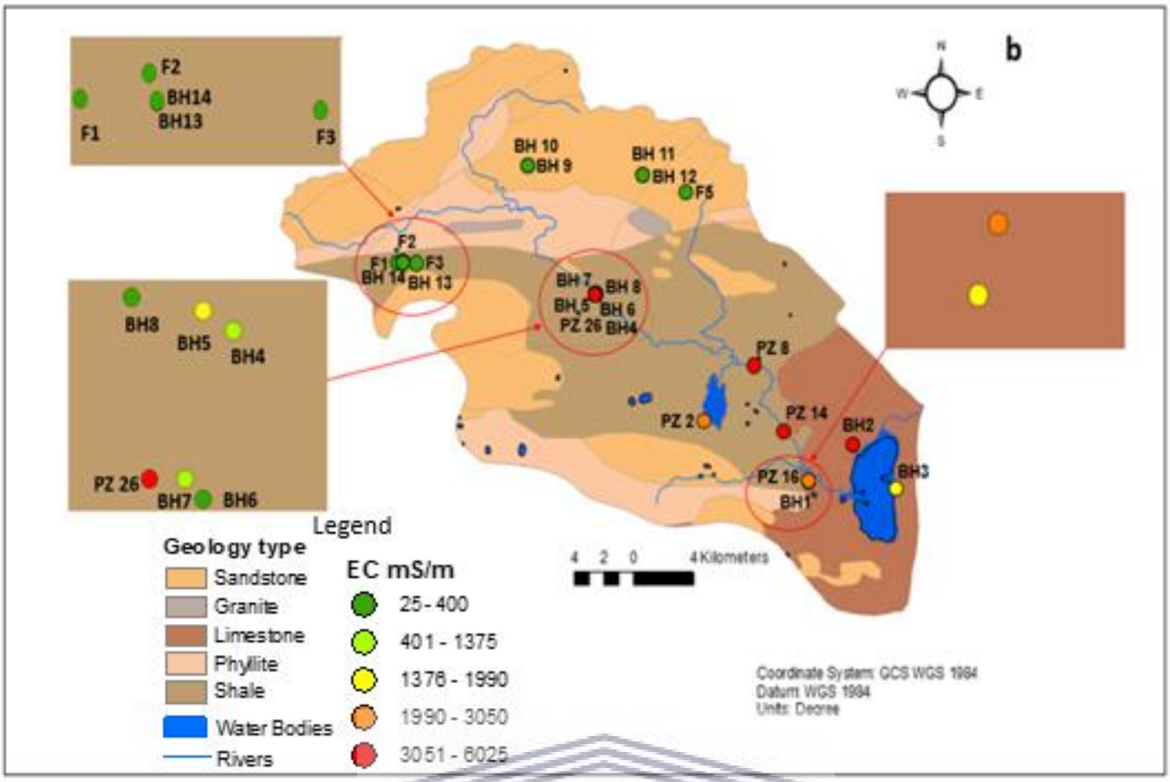


Figure 13: Spatial distribution of average EC in groundwater (July2017- July 2018), (a) not related to geology (b) related to geology.

5.2.5 Major ions

5.2.5.1 Cation-anion balance

The cation-anion balance (CAB) results, previously discussed in the reliability and validity section of this thesis, are presented in Table 6. Results indicate that 7 of a total of 33 samples in July 2017, 8 of 32 samples in October 2017, 6 of 34 samples in March 2018 and 4 of 37 samples in July 2018 exceeded the recommended maximal error of ±15%. The data obtained for these samples can therefore not be validated. Although discussed with caution in the description of temporal and spatial trends of water quality parameters, results obtained from these particular water samples were not included in the generation of the piper diagram and bivariate plots.

The pattern of errors appears to be random in that the error in most samples was not consistent and occurred only once, except for samples NJ1, NJ2 and PZ8. Although many factors can result in a CAB above the acceptable range, the error for samples that only yielded a CAB above ± 15% once can be attributed to either sampling errors or an error during laboratory analysis. Further investigation and monitoring is required for sites, (NJ1, NJ2 and PZ8) to identify the source or sources of the error.

Table 6: Cation-anion balance (CAB) results

Site ID	July (2017)	October (2017)	March (2018)	July (2018)
NJ 1	12.7	-18.6	-55.6	-22.6
NJ 2	8.6	-2.2	-57.4	-27.8
NJ 3	4.3	-2.6	-3.8	-13.8
NJ 4	8.8	-1.5	0.1	-4.4
NJ 5	18.6	1.8	-7.0	-4.9
NJ 6	64.9	4.0	1.9	3.1
NJ 7	1.0	0.5	3.3	2.3
NJ 8	9.7	-0.5	0.4	1.1
VOB	13.3	2.5	-29.2	-4.0
PT 1	-2.4	-0.2	4.6	8.6
JS1		-3.0	-0.1	9.8
ETS			1.3	5.7
F1	0.0	-2.7	0.7	8.1
F2	-1.0	7.5		3.9
F3	-21.1	-0.1	-4.0	-0.4
F4	-0.7			
F5	-7.5	-5.6	3.4	-6.5
BH1	9.2	-8.6	-11.3	-4.2
BH2			-82.7	-7.8
BH3	2.0		-82.6	0.0
BH4	0.2	-21.3	-4.7	9.0
BH5	1.9	-24.8	-0.3	12.3
BH6	6.2	-11.9	1.7	75.3
BH7	11.8	-9.1	-12.6	12.7
BH8	6.2	-7.5	-11.7	-7.2
BH9	-19.6	-4.9	-16.7	-9.6
BH10	4.5	5.8	-8.9	8.5
BH11	9.8	-28.5	-8.1	0.5
BH12	12.9	-4.8	2.5	30.5
BH13	-17.8	-6.3	-6.6	9.6
BH14	-4.9	2.4	-0.9	7.8
PZ2		-12.2	-11.1	-5.3
PZ 7	-12.3			
PZ 8	-70.8	-69.7	-2.7	3.7
PZ 13	-38.6			
PZ 14	5.2	-79.0	-11.2	-11.3
PZ16		-53.0	-3.8	-9.3
PZ 19	6.3			
PZ26		-82.5	-7.9	1.0
SBH				5.3
RFM				-2.0

5.2.5.2 Major ions

Results obtained from the hydrochemical analysis conducted on groundwater and surface water in the Nuwejaars Catchment are presented in Table 7. The results indicate that, major ions in waters of the Nuwejaars Catchment were present in the following order of abundance, $Cl^- > Na^+ > Mg^{2+} > SO^{2-}_4 > Ca^{2+} > HCO^-_3 > K^+$, throughout the sampling period. Although, the magnitude, pattern and trends of concentrations of each of the major ions are included within this section, sodium and chloride are discussed in greater detail. This is particularly because, sodium and chloride are conservative ions and are usually the dominant ions in waters within the region of the study area. Results from the significance tests reported on in this chapter are presented in Appendix 7.

Table 7: Statistical summary of major ion concentrations in the Nuwejaars Catchment, July 2017-July 2018 (Units: meq/L).

5.2.2.1.1	Surface water (n=10)		b) Deep Groundwater (n=15)						
Parameter	**Sampling month**	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Sodium	July (2017)	3.3	98.5	44.5	35.2	1.9	112.0	31.9	40.8
	October (2017)	4.7	95.7	19.5	30.4	1.8	52.0	15.4	17.5
	March (2018)	4.7	55.9	27.0	21.3	1.8	123.3	28.2	42.0
	July (2018)	4.6	358.9	78.7	116.5	1.6	348.0	91.4	133.8
Calcium	July (2017)	0.2	5.6	2.4	2.0	0.1	9.5	1.7	2.4
	October (2017)	0.4	4.9	1.3	1.6	0.2	6.4	1.2	1.7
	March (2018)	0.3	7.6	2.9	2.8	0.1	7.3	1.9	2.4
	July (2018)	0.2	19.6	6.3	8.0	0.0	12.8	3.6	4.9
Potassium	July (2017)	0.0	0.8	0.3	0.3	0.1	2.0	0.3	0.5
	October (2017)	0.1	0.8	0.2	0.3	0.0	0.5	0.1	0.2
	March (2018)	0.0	1.3	0.4	0.5	0.2	0.7	0.1	0.2
	July (2018)	0.1	1.6	0.4	0.5	0.0	1.5	0.2	0.4
Magnesium	July (2017)	1.0	14.8	7.4	5.3	0.4	13.2	4.2	5.1
	October (2017)	1.5	14.0	4.2	5.0	0.3	11.5	3.2	3.7
	March (2018)	1.3	19.8	8.5	7.0	0.4	16.5	4.2	5.8
	July (2018)	1.2	43.6	15.0	16.2	0.3	33.7	8.3	12.0
Chloride	July (2017)	4.0	91.0	37.7	34.3	2.5	114.8	30.4	40.6
	October (2017)	5.9	104.3	24.9	37.5	2.4	95.2	23.3	30.2
	March (2018)	5.3	284.6	78.5	103.6	2.5	132.7	32.9	48.2
	July (2018)	4.4	520.0	130.2	186.2	1.7	391.7	69.5	116.4
Sulphate	July (2017)	0.4	7.1	3.3	2.3	0.0	13.4	2.8	4.2
	October (2017)	0.0	8.6	2.0	3.3	0.0	12.5	2.5	3.8
	March (2018)	0.2	17.4	4.3	5.7	0.1	19.5	4.0	6.8
	July (2018)	0.6	27.4	9.1	11.1	0.0	19.1	4.1	6.6
Bicarbonate	July (2017)	0.3	3.6	1.3	1.2	0.1	4.0	1.5	1.3
	October (2017)	0.2	6.4	1.2	1.9	0.1	3.6	1.3	1.2

	March (2018)	0.1	7.8	3.0	2.8	0.2	5.2	1.8	1.6
	July (2018)	0.2	6.6	1.7	2.0	0.2	5.6	1.6	1.7

b) Shallow Groundwater Units: meq/L (n=5)

Parameter	Sampling month	Min	Max	Mean	SD
Sodium	July (2017)	48.2	114.2	81.2	46.7
	October (2017)	45.6	290.3	170.8	107.7
	March (2018)	135.2	501.7	220.1	156.1
	July (2018)	353.4	706.8	475.8	170.1
Calcium	July (2017)	3.5	12.4	8.0	6.3
	October (2017)	4.3	21.5	9.7	6.8
	March (2018)	4.1	27.7	7.8	10.0
	July (2018)	11.9	37.5	18.0	11.4
Potassium	July (2017)	1.0	1.4	1.2	0.3
	October (2017)	0.9	2.0	1.5	0.5
	March (2018)	0.4	0.7	0.4	0.2
	July (2018)	0.1	1.2	0.9	0.4
Magnesium	July (2017)	15.6	23.9	19.7	5.8
	October (2017)	18.1	24.7	23.0	2.8
	March (2018)	12.3	45.3	22.6	15.0
	July (2018)	35.4	47.7	39.5	5.7
Chloride	July (2017)	113.4	462.8	288.1	247.1
	October (2017)	215.8	775.1	482.3	217.4
	March (2018)	152.2	622.9	353.7	201.0
	July (2018)	433.0	929.7	630.3	199.2
Sulphate	July (2017)	6.2	7.2	6.7	0.7
	October (2017)	10.0	49.6	31.8	17.3
	March (2018)	7.6	49.0	29.3	16.9
	July (2018)	10.1	45.8	29.5	15.1
Bicarbonate	July (2017)	1.6	2.7	2.1	0.8
	October (2017)	2.5	5.1	3.4	1.2
	March (2018)	2.9	6.0	4.2	1.4
	July (2018)	2.0	4.8	3.4	1.3

5.2.5.3 Chloride and Sodium

Chloride and sodium were the dominant ions, present in all waters of the Nuwejaars Catchment. Similar trends in concentrations of sodium and chloride during the sampling period can be observed in Figure 14. In surface water, chloride and sodium concentrations were variable, ranging between 4.0 and 520 meq/L, and 3.3 and 358 meq/L, respectively, during the study period. No significant temporal changes in sodium (F (3, 27) = 2.7, p value = 0.06) and chloride (F (3, 27) = 2.7, p value = 0.07) concentrations of surface water were identified from the statistical tests, however lower concentrations in surface water were recorded in October 2017 (Figure 14).

The lowest mean of 24.9 meq/L for chloride and the lowest mean of 19.5 meq/L for sodium were recorded during October 2017 after the end of the wet season. Lower concentrations during this period can be attributed to increased flows after the wet season and dilution within the river. No significant changes in sodium (t (9) = -1.01, p value= 0.34) and chloride (t (9) = -0.87, p value = 0.4) concentrations between the upper and lower sections of the river were observed during this period. The increase in mean values, from 24.9 to 78.5 meq/L in chloride and 19.5 to 27.0 meq/L in sodium between October 2017 and March 2018, a period, which marked the peak of the drought, gives an indication of decreased flows and reduced dilution within the river.

The standard deviations (SD) computed, indicate that the greatest variability in sodium and chloride concentrations of surface water within the catchment were experienced in July 2018. Computed SD values for this season were as high as 116.5 and 186.2 for sodium and chloride respectively, values far greater than those computed for July 2017- March 2018. Statistical tests indicate that surface water chloride and sodium concentrations in the upper and lower sections of the catchment varied significantly during July 2018 (t (9) = 3.54, p value = 0.006) for sodium and (t (9) =3.75, p value = 0.005) for chloride, while no differences in concentrations were observed between these two regions during July and October 2017. The wet season of July 2018 also recorded the highest concentrations in surface waters, with mean values of 130.2 meq/L for chloride and 78.7 meq/L for sodium, after a number of rainfall events following the extreme dry period.

Chloride and sodium concentrations in the Nuwejaars Catchment, were lower in deep groundwater than in shallow groundwater. Values for chloride ranged between 1.7 and 391.7 meq/L in deep groundwater and 113.4 and 929.7 meq/L in shallow groundwater, while values for sodium ranged between 1.6 and 348 meq/L in deep ground water and between 45.6 and 706.8 meq/L in shallow ground water. Sodium concentrations in deep groundwater varied over time (F (1, 19) = 6.92, p value = 0.01), while no significant differences were observed in chloride concentrations (F (1, 21) = 1.7, p value = 0.21) during the study period. These trends can be observed on Figure 14b and 14d. Outliers are representative of the elevated chloride and sodium concentrations detected in piezometers and boreholes located downstream in the limestone region of the catchment. The largest mean of 91.4 meq/L and SD of 133.8, for sodium, and a mean of 69.5 meq/L and SD of 116 for chloride in deep groundwater were recorded in July 2018, as was for surface water. This suggests that, the highest concentrations of both ions were recorded during this season and greater variability in the concentration of sodium and chloride in deep groundwater were observed during this period.

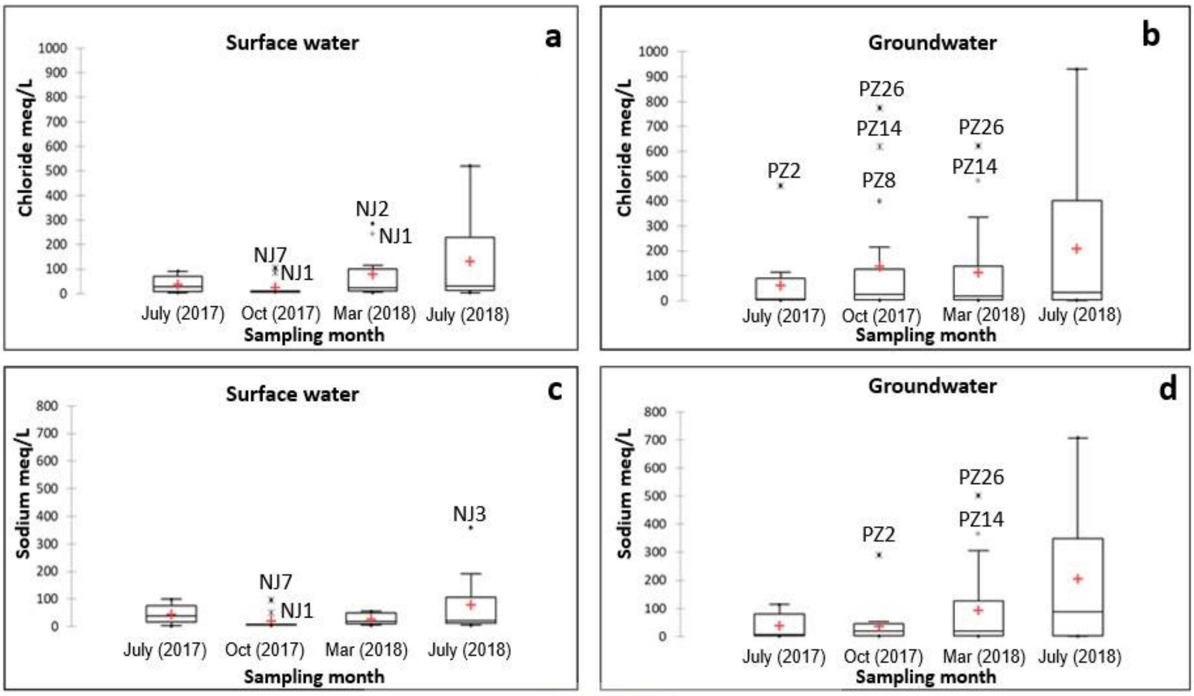


Figure 14: Boxplots of sodium and chloride concentrations of surface water (n= 10) and groundwater (n= 20).

During the wet season, dilution within the river is expected, however, at the time of sampling in July 2018, only a few rainfall events had occurred. The month of July 2018 received less rainfall as compared to the amount of rainfall received in July 2017. Prior to the sampling campaign in July 2018, the area experienced drought conditions with high temperatures and little to no rain. As a result, a limited amount of rainfall (below 30mm) was received between December 2017 and July 2018 for the majority of the catchment, with the exception of Tierfontein in the recharge area that received rainfall amounts up to 86.6mm in June 2018. Although rainfall data for Moddervlei is incomplete and does not include rainfall records for June and July 2018, rainfall amounts at this weather station were usually higher than those recorded at Vissersdrif downstream. The amount of rainfall received each month, during the study period is presented in Figure 3. There is a possibility that little runoff was generated prior to sampling in July 2018 and that most of the rain from the first few rainfall events infiltrated into the very dry ground until soils were saturated, before runoff could be generated. It is therefore plausible that a limited amount of dilution actually occurred during this period, although not usually expected during the wet season, resulting in increased concentrations of salts. This is however dependent on the rainfall intensity, rainfall of high intensity favouring runoff over infiltration, and rainfall of low intensity favouring infiltration (Linsley, 2009). Elevated chloride and sodium concentrations during the wet season can also indicate a substantial amount of solutes entering the river in the form of runoff. Precipitation of a Na-Cl type, such as that received within the catchment can also contribute to the concentrations measured during the wet season.

Shallow groundwater recorded higher concentrations of sodium and chloride as compared to deep groundwater because, before reaching the aquifer, water travels through the unsaturated zone were plant roots and soils are present, which act as a buffer. As a result, when rain water finally recharges the aquifer it is diluted and its chemistry would have been altered. According to Britton and Day (1993), the residence and percolation time of rainwater in soil profiles is longer during dry periods, hence lower concentrations of solutes during the dry season can be expected in deep groundwater. This explains the lower concentrations of sodium and chloride recorded during the drier seasons.

The spatial distribution of average chloride and sodium concentrations of surface water across the catchment are presented in Figure 15. Solutes generally accumulate downstream of a river (DWAF, 1996), hence chloride and sodium concentrations in the Nuwejaars Catchment also increased downstream (see Figure 15). River sites NJ1, NJ2 and NJ3, located downstream, recorded the highest concentrations. These sites are located, near the coast, at low elevations, in a previously marine environment. Saline deposits and sea sprays in coastal catchments can also influence water chemistry (Laar, 2018), elevating concentrations of chloride in particular. Although sodium is naturally occurring, elevated concentrations such as those measured during the study period, also suggest the possibility of sodium entering the system from other sources, such as return flows from agricultural farming (Dinka et al., 2015), although this has not been reported on or confirmed.

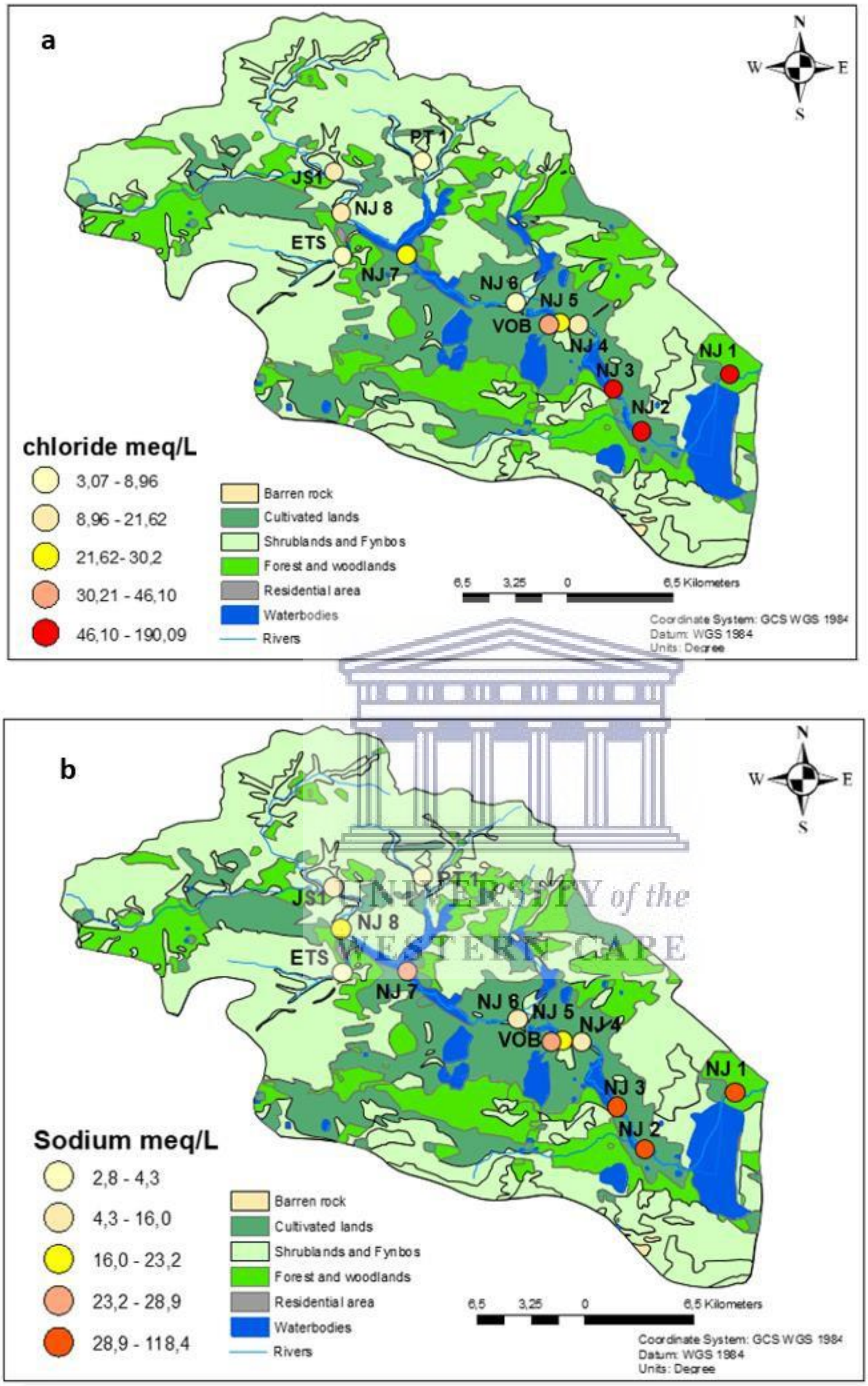


Figure 15: Spatial distribution of average (a) chloride and (b) sodium concentrations in surface water related to land use (July 2017- July 2018).

The spatial distribution of chloride and sodium concentrations in groundwater are presented in Figure 16. Sodium and chloride concentrations in deep groundwater varied between the upper and lower regions of the catchment (p values < 0.001). Chloride concentrations in deep groundwater upstream in the sandstone region of the catchment were lower, recording values below 10 meq/L, while the sections further downstream, underlain by shale and limestone, yielded higher concentrations, well above 100 meq/L, particularly in 2018. Variations in chloride concentrations in groundwater in the Nuwejaars Catchment can therefore be attributed to the nature of the underlying lithology and groundwater residence time. As previously explained, groundwater flow downstream is limited, hence the increased concentrations of salts in this region, due to longer residence times.

The spatial distribution of sodium concentrations in groundwater were variable in the middle and lower regions of the catchment, therefore, unlike for chloride, no particular trend in concentrations, or relationship between sodium abundance and geological type, could be observed. Increased salinity levels downstream of the catchment can also be attributed to ancient groundwater, rich in chloride that derived as sea water, entering the aquifer at a time when the height above sea level was different (Younger, 2007).

According to Day and King (1995) and Gibbs (1970), waters dominated by sodium and chloride in regions where the TMG sandstones of the Cape Super Group dominate, are diluted precipitation dominated waters. This is true in the upper sections of the Nuwejaars Catchment, were fresh waters are prominent particularly due to the TMG formation that underlies the region. However, further downstream, in the Bokkerveld shale and Bredasdorp calcified sands and limestone regions, where waters characterised by high sodium and chloride concentrations dominate, other processes such as evaporation and rock-water interactions affect water chemistry to a greater extent.

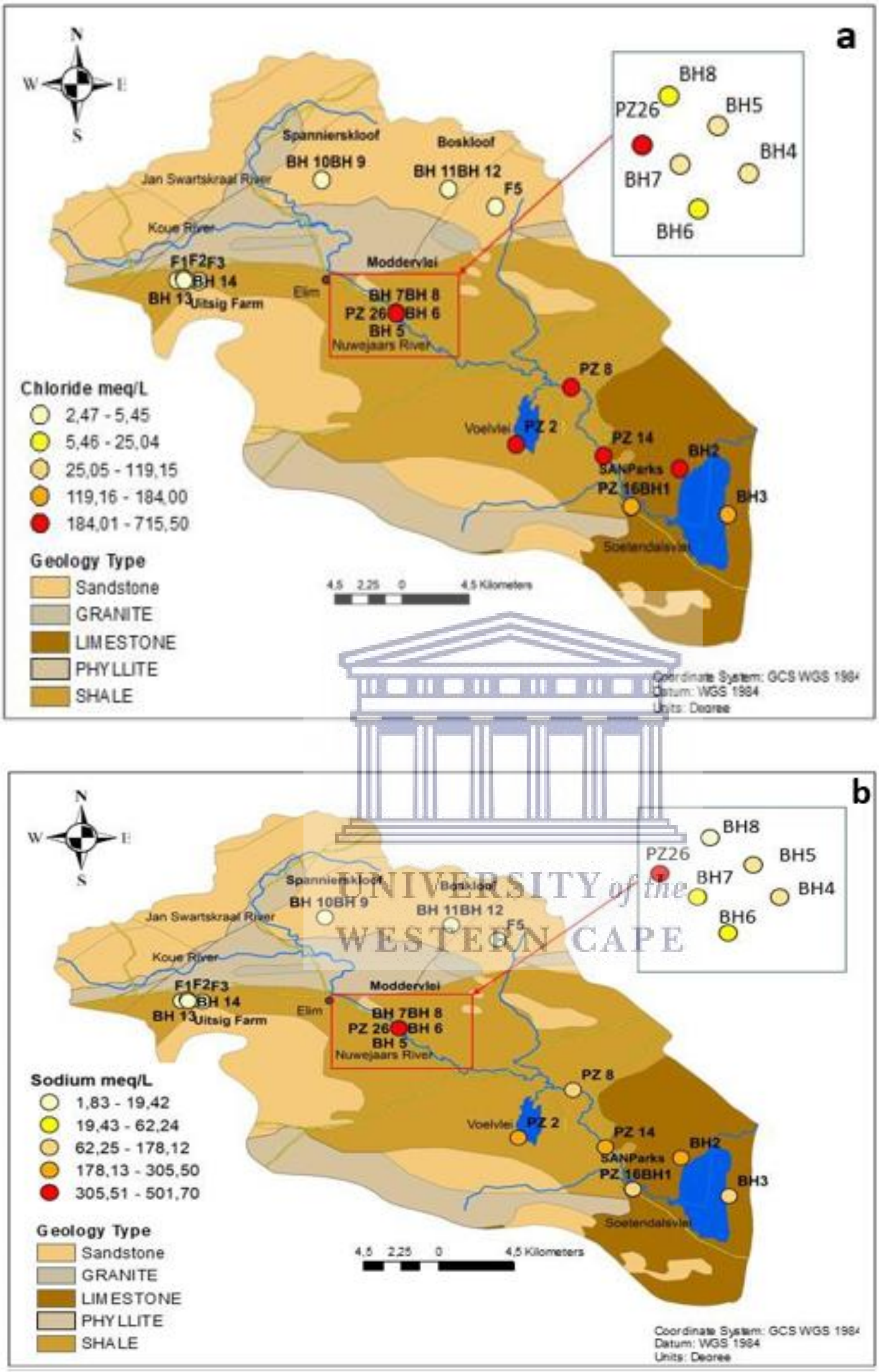


Figure 16: Spatial distribution of average (a) chloride and (b) sodium concentrations in shallow and deep groundwater related to geology (July 2017- July 2018).

5.2.5.4 Calcium and Magnesium

The results obtained indicate no significant temporal variations in calcium concentrations of surface water (F (1, 13) =3.16, p value = 0.09) and deep groundwater (F (2, 21) = 1.72, p value = 0.2) in the Nuwejaars Catchment during July 2017 – July 2018. Calcium concentrations ranged between undetectable and 37.5 meq/L for all waters of the Nuwejaars Catchment. Concentrations in deep groundwater and surface water were generally below 10 meq/L, while average concentrations in shallow groundwater were up to 18 meq/L. Magnesium was more abundant than calcium, with concentrations ranging between 0.33 and 47.7 meq/L for all waters. Shallow groundwater yielded the highest average magnesium concentration of 39.5 meq/L.

Concentrations of magnesium in surface water did not change significantly over time (F (2, 24) = 3.43, p value = 0.07), however temporal variations in deep groundwater were observed (F (2, 28) = 4.39, p value = 0.02). As for the ions discussed in other sections, the highest concentrations of both calcium and magnesium in surface water and groundwater were detected in July 2018 during the wet season (see Figure 17), while the lowest concentrations were measured in October 2017 at the onset of the dry season. Although not as variable as sodium and chloride, the largest and smallest SD values for all waters were also computed for July 2018 and October 2017, suggesting that concentrations were more variable during the wet season of 2018. Temporal variations of calcium and magnesium concentrations during the study period are presented in Figure 17.

It was expected that concentrations of calcium and magnesium would not surpass those for sodium and chloride within the study area. This is because, during the process of evaporation, calcium and magnesium ions precipitate out first, leaving sodium and chloride in solution, hence these ions exist in lower concentrations in arid regions (Day and king 1995). Although calcium and magnesium ions are generally found in low concentrations in the south-west regions of South Africa (Day and King, 1995), concentrations in all waters were higher in the lower sections of the catchment, particularly within the limestone region. This was expected because, Calcium and magnesium are naturally occurring as a result of the dissolution of carbonates such as calcite and dolomite, minerals that are abundant in regions dominated by limestones (Kresic, 2006; Younger, 2007). Due to differences in geology, deep groundwater in the upper catchment within the Table Mountain Group region and deep groundwater in the lower catchment within the limestone region exhibited distinct variations in calcium and magnesium concentrations during the study period (p values below 0.05).

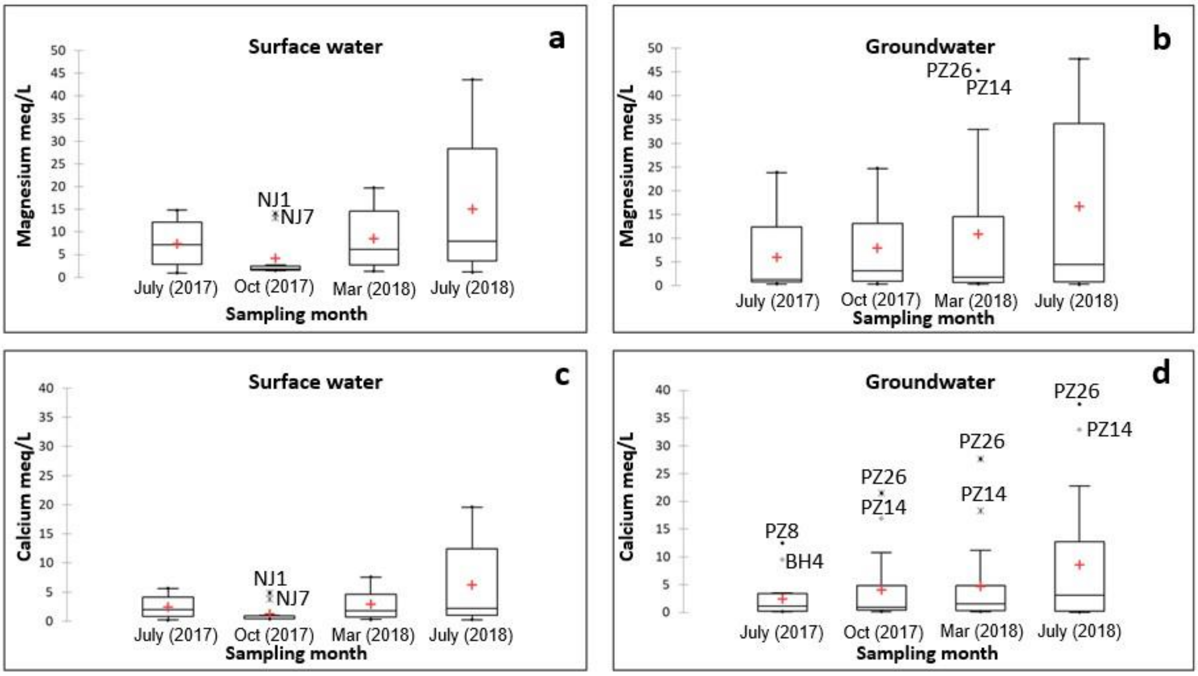


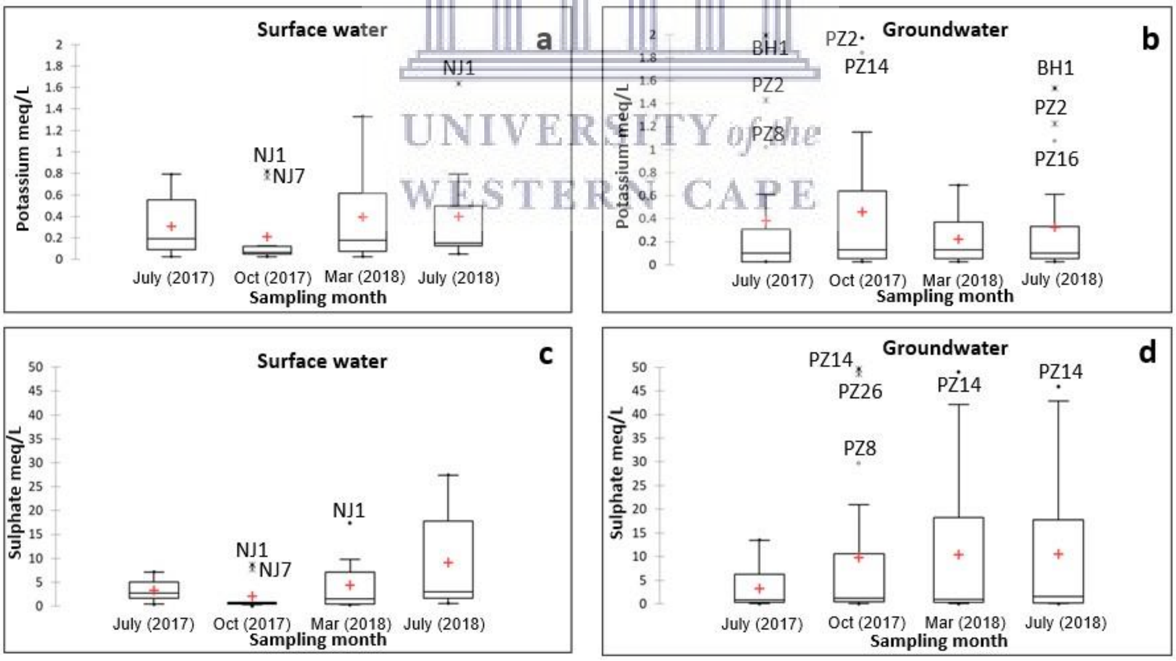
Figure 17: Boxplots of calcium and magnesium concentrations of surface water (n= 10) and groundwater (n= 20).

5.2.5.5 Sulphate, Bicarbonate and Potassium

Sulphate and potassium in surface water and deep groundwater did not vary significantly during the four sampling campaigns (p values above 0.05). On the contrary, temporal variations in bicarbonate concentrations for both surface water (F (3, 27) = 3.03, p value= 0.046) and groundwater (F (3, 42) = 4.41, p value = 0.01) were identified. Sulphate concentrations in all waters ranged between undetectable and 49.6 meq/L, during the sampling period. In surface water, sulphate concentrations were usually below 10 meq/L, however, higher values up to 27.4 meq/L were measured on occasion. In surface waters, mean sulphate concentrations ranged between 2.0 and 9.1 meq/L, with the lowest and highest concentrations recorded in October 2017 and July 2018 respectively (see Figure 18c).

In deep groundwater, sulphate concentrations averaged between 2.5 and 4.1 meq/L, although concentrations as high as 19.5 meq/L were measured. The highest concentrations were measured in shallow groundwater, with a maximum concentration almost as high as 50 meq/L being recorded in a piezometer in the lower sections of the catchment, while mean values generally ranged between 6.75 and 31.78 meq/L. According to Dallas and Day (2004) sulphate is naturally occurring as a result of the association of waters and rocks containing gypsum and anhydrite. Sulphate ions normally occur in lower concentrations as compared to either bicarbonate or chloride ions, in natural waters. In this case sulphate ions occurred in concentrations lower than those recorded for chloride.

Bicarbonate and potassium ions recorded the lowest concentrations in all waters of the Nuwejaars Catchment as compared to the other ions, ranging between 0.1 and 7.77 meq/L and 0.03 and 2.0 meq/L respectively. Temporal variability of bicarbonate concentrations in groundwater were less pronounced as compared to surface water (see Figure 18e and f). Bicarbonate and potassium concentrations in all waters were generally higher in the lower sections of the catchment, within the limestone region. Much like calcium and magnesium, bicarbonate ions in groundwater, form as a result of the dissolution of carbonate rocks such as limestones, dolomites, magnesites. According to Elango and Kannan (2007) the presence of bicarbonate ions suggests that processes of silicate and carbonate weathering are present and influence groundwater chemistry within the catchment. Although similar to sodium in terms of magnitude and solubility, unlike sodium, potassium is usually present in low concentrations in surface waters. This is because potassium, promotes biological processes in plants and micro- organisms, hence its low presence in waters (Dinka et al., 2015). The majority of the outliers presented in figure 18 are representative of waters located downstream within the limestone region of the catchment. As previously mentioned, concentrations of calcium, magnesium and bicarbonate ions are expected to be higher in limestone dominated regions.



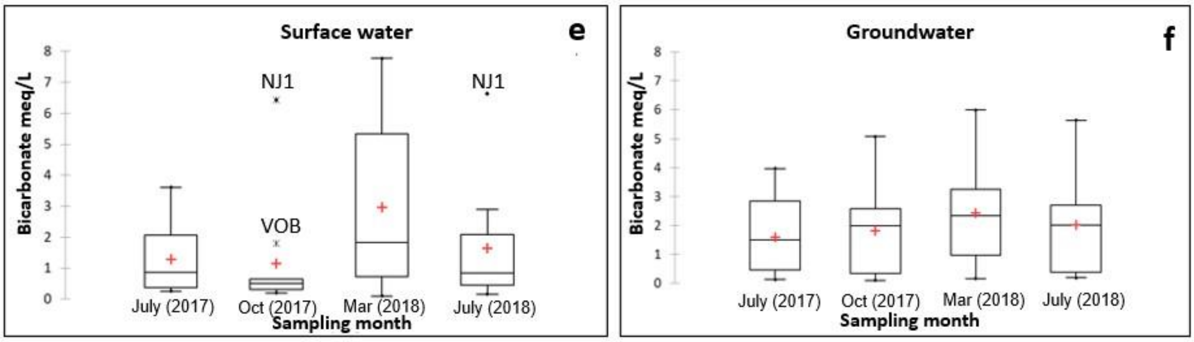


Figure 18: Boxplots of sulphate, bicarbonate and potassium concentrations of surface water (n= 10) and groundwater (n= 20).

5.2.6 Nutrients

Nutrient concentrations recorded for surface water and groundwater during the study period are presented in Table 8. The information below, provides a summary of the data obtained, detailed results are presented in Appendix 2. Results from the significance tests reported on in this section are also presented in Appendix 7.

Table 8: Statistical summary of nutrient concentrations in groundwater and surface water.

a) Surface water Units: mg/L (n=10)

Parameter	Sampling month	Min	Max	Mean	SD
Nitrate	July (2017)	0.1	0.7	0.2	0.2
	October (2017)	<0.1	0.3	0.1	0.1
	March (2018)	0.1	0.6	0.3	0.2
	July (2018)	<0.1	0.7	0.2	0.2
Total nitrogen	July (2017)	0.2	2.0	0.7	0.5
	October (2017)	0.3	0.5	0.5	0.1
	March (2018)	0.4	4.4	1.0	1.2
	July (2018)	0.1	2.9	0.8	0.8
Phosphate	July (2017)	0.3	2.3	1.7	0.6
	October (2017)	1.4	3.6	2.6	0.6
	March (2018)	0.2	18.6	3.6	6.0
	July (2018)	1.0	3.7	1.7	0.7
Total Phosphorus	July (2017)	0.7	2.7	2.1	0.5
	October (2017)	1.9	3.8	2.9	0.6
	March (2018)	0.5	20.0	4.2	6.2
	July (2018)	1.3	3.9	2.0	0.8

b) Deep Groundwater Units: mg/L (n=15)

Parameter	Sampling month	Min	Max	Mean	SD
Nitrate	July (2017)	<0.1	0.8	0.3	0.2
	October (2017)	0.1	1.5	0.4	0.4
	March (2018)	<0.1	1.0	0.4	0.3
	July (2018)	<0.1	1.5	0.3	0.4

Total nitrogen	July (2017)	<0.1	5.1	1.0	1.4
	October (2017)	0.3	1.6	0.7	0.4
	March (2018)	0.3	3.0	0.7	0.6
	July (2018)	0.1	36.7	3.3	9.0
Phosphate	July (2017)	<0.1	74.0	8.1	18.9
	October (2017)	0.4	22.6	4.8	7.2
	March (2018)	<0.1	3.3	1.0	1.1
	July (2018)	0.3	7.7	2.1	2.1
Total Phosphorus	July (2017)	0.1	25.0	4.3	7.4
	October (2017)	0.6	22.5	5.0	7.1
	March (2018)	0.1	3.9	1.4	1.2
	July (2018)	0.6	8.3	2.4	2.1

c) Shallow groundwater Units: mg/L (n=5)

Parameter	Sampling month	Min	Max	Mean	SD
Nitrate	July (2017)	0.1	3.0	1.3	1.1
	October (2017)	0.2	1.0	0.7	0.3
	March (2018)	0.2	1.0	0.6	0.3
	July (2018)	0.3	0.6	0.5	0.1
Total nitrogen	July (2017)	0.1	3.2	1.3	1.2
	October (2017)	0.4	3.4	1.6	1.1
	March (2018)	0.5	1.3	0.8	0.3
	July (2018)	0.6	41.2	15.9	16.8
Phosphate	July (2017)	1.8	3.5	2.7	0.8
	October (2017)	0.8	6.3	3.7	2.5
	March (2018)	0.1	0.4	0.2	0.1
	July (2018)	0.7	2.1	1.6	0.5
Total Phosphorus	July (2017)	1.9	4.0	3.0	0.9
	October (2017)	2.1	8.3	4.9	2.7
	March (2018)	0.3	0.8	0.6	0.2
	July (2018)	0.6	3.1	2.0	0.9

5.2.6.1 Nitrate and Total Nitrogen

Nitrate concentrations in surface water and groundwater in the Nuwejaars Catchment were present in low amounts during July 2017-July 2018. Concentrations usually fell between undetectable and below 1 mg/L for both groundwater and surface water. However, the highest recorded concentrations, from shallow groundwater were up to 3 mg/L. Shallow groundwater and deep groundwater that recorded nitrate concentrations above 1mg/L are the outliers visible in Figure 19b. Nitrate concentrations recorded at these locations were still within acceptable limits as stipulated by the South African Water Quality Guidelines. Nitrate concentrations did not vary both spatially and temporally (p values greater 0.05). Concentrations of nitrate recorded during the study period suggest that agricultural activities within the catchment do not largely influence water chemistry.

Total nitrogen (TN) concentrations in the Nuwejaars Catchment, ranged between undetectable and 41.2 mg/L, exceeding the minimum and maximum detection limits. Increased concentrations were particularly observed in July 2018, during the wet season, with values above 25 mg/L being recorded during this season. Mean concentrations recorded during the duration of the study for surface water measured less than 1mg/L. However, on occasion, concentrations greater than 1 mg/L were recorded (See Appendix 2). The standard deviations of surface water, in the dry and wet season of 2018 were larger than those computed for 2017. This gives an indications that surface water TN concentrations in March and July 2018 were more variable that those recorded in 2017. These variations were however not statistically significant, results indicate that TN concentrations in both surface water and groundwater did not vary significantly during the study period (p values greater than 0.05).

In July 2018, water samples collected from a pool at river site JS1, exhibited increased concentrations (4.2 mg/L) as compared to the rest of the surface water sites. This can be attributed to the stagnation of water at this site, which does not promote dilution. Occasional increases in TN concentrations such as those recorded only during July 2018 are less important than continuously high concentrations being recorded at a specific site (DWAF, 1996). TN concentrations recorded during the study period, with the exception of occasional once off increases, suggest that nutrient concentrations in rivers of the Nuwejaars Catchment do not largely promote the growth of blue-green algae and other plants that may alter the quality of river waters.

TN concentrations of deep groundwater were also generally measured below 1 mg/L, with the exception of the wet season of July 2018, while shallow groundwater measured concentrations up to 41.2 mg/L. Shallow groundwater samples from PZ8 yielded the highest recorded TN concentration of 41.2 mg/L, while PZ16 consistently recorded TN concentrations above 3mg/L and even up to over 15 mg/L, during the wet season of 2018. Increased TN concentrations in groundwater recorded during the July 2018, downstream, can be attributed to the infiltration of pollutants during the rainfall events that occurred prior to sampling.

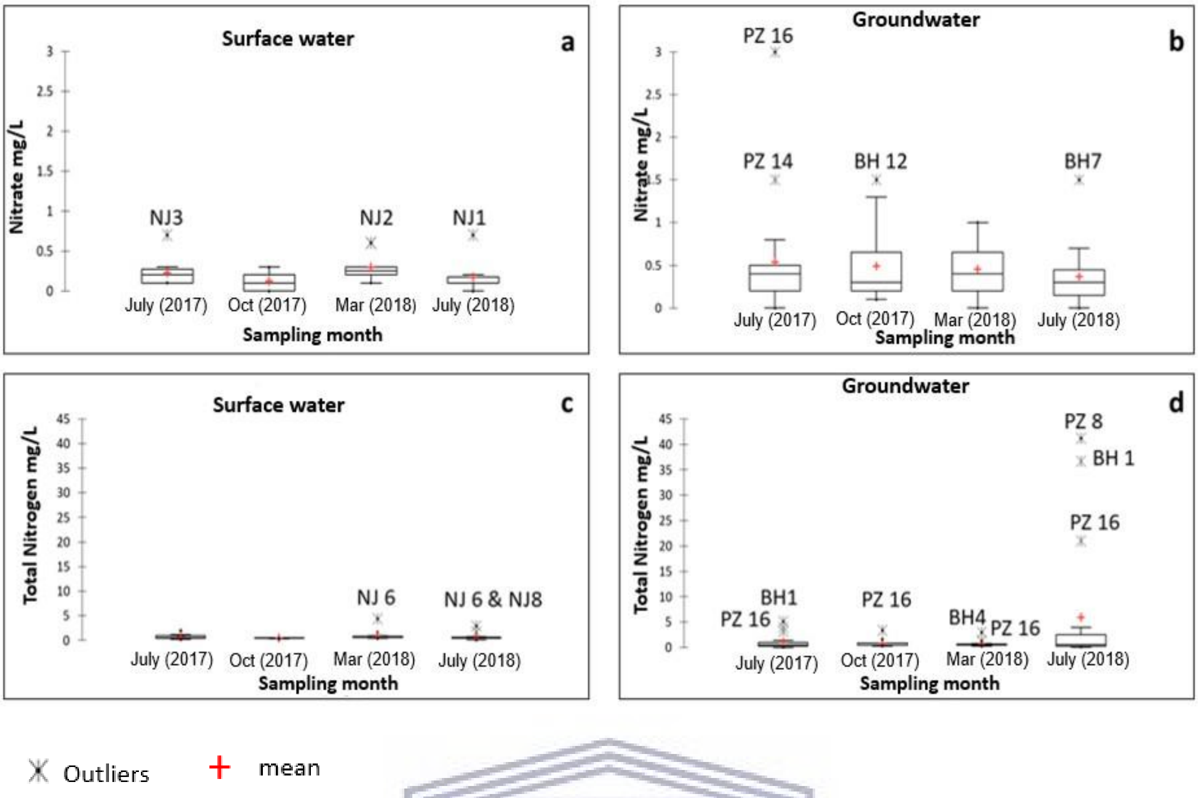


Figure 19: Concentrations of nitrate and total nitrogen in surface water (n= 10) and groundwater (n=20), during the study period.

5.2.6.2 Phosphate

Phosphate concentrations in surface water ranged between 0.2 and 18.6 mg/L, during the sampling period. The highest concentrations were recorded during the dry season of March 2018, with concentrations above 10 mg/L being recorded at particular sites along the river (NJ2 and VOB). On the contrary, the lowest phosphate concentrations in surface water, were measured during the wet seasons, at concentrations usually below 2 mg/L. Slight variations in phosphate concentrations recorded for surface water during the study period can be observed from Figure 20a. However these temporal variations were not significant (p values greater than 0.05). During the dry season two sites in particular recorded high phosphate concentrations, NJ2 at 18.6 mg/L, and VOB at 11 mg/L, these two are outliers in the box plot (Figure 20a). Regardless of the outliers presented in figure 20a, no considerable differences in surface water phosphate concentrations could be observed both spatially and temporally (p values greater than 0.05).

Phosphates in groundwater ranged between undetectable and 74 mg/L. This high maximum value may be as a result of experimental error, however BH13 at the same location also recoded a value of 25.7 mg/L, during the same period. Similar concentrations at these sites were during both the dry and wet season of 2017. High concentrations at this location can be attributable to contamination from a nearby cattle feed-lot, during this period. The computed standard deviations suggest that phosphate concentrations in groundwater were more variable than those recorded for surface water, throughout the sampling period.

5.2.6.3 Total Phosphorus

Total Phosphorus (TP) concentrations in surface water ranged between 0.5 and 20 mg/L, during July 2017 and July 2018. The highest mean recorded for surface water TP was 4.20 mg/L in March 2018, during the driest period, while the lowest mean of 2 mg/L was recorded in July 2018 during the wet season. Lower TP concentrations in the wet season can be attributed to the effects of the dilution process that takes place during the wet season when more rainfall is received. No significant differences in TP (p values greater than 0.05) during the sampling period were observed from upstream to downstream, although NJ2 exhibited the highest TP value of 20 mg/L, while VOB, at the Voelvlei outlet, recorded a TP value of 11.8 mg/L, during March 2018. Concentrations recorded at these 2 sites, are primarily responsible for the high mean value recorded during March 2018 as compared to the rest of the sampling periods. High TP concentrations at these sites during summer can be attributed to reduced flows and a limited amount of dilution within the river.

TP concentrations in deep groundwater did not vary considerably during the sampling period (p values greater than 0.05). Figure 20d, shows slight variations in concentrations recorded between the 4 sampling campaigns. Concentrations recorded upstream and downstream also did not show major differences (p values greater than 0.05), regardless of the occasional increases detected. TP concentrations in deep groundwater generally range between 0.1 and 25 mg/L. In October and July 2017, the highest means of 5.0 and 4.3 mg/L were recorded respectively, while the lowest mean of 1.4 mg/L was recorded in March 2018, which is different from the situation in surface water. In July and October 2017, three boreholes (BH1, BH13 and BH14) exhibited values significantly higher than the rest of the boreholes; these are the three outliers in the box plot in Figure 20d. In March and July 2018 the measured TP concentrations for these sites fell within range of values for the majority of the boreholes. BH13 and BH14 are located at the same site upstream at Uitsig farm and BH1 is located downstream. Higher TP concentration during the two sampling campaigns might be attributable to contaminants from the farm. Shallow groundwater also recorded slightly higher TP concentrations as compared to the rest of the boreholes across the catchment, with the exception of the three boreholes discussed above (BH1, BH13 and BH14). Shallow groundwater therefore contained more phosphorus than deep groundwater, primarily because soils and plant roots near the surface, within the depth at which shallow groundwater was sampled trap sediments and nutrients.

Although, concerns of pollution from farming activities that take place near the floodplain of the river in the study area have been highlighted in a recent report by Mazvimavi (2017), the results obtained by the current study, with the exception of occasional increases detected at particular sites, do not confirm that farming activities negatively impact the chemistry of rivers within the catchment. Surface water sites that did show some fluctuations, did not record consistent increased values of nutrient concentrations over time. Increased concentrations at particular sites can therefore be attributed to once off occurrences of contamination. Deep groundwater upstream (BH13 and BH14), sampled from a cattle farm, did however record increased phosphate concentrations during the wet and dry season of 2017. The influence of livestock productions at this location may be responsible for these concentrations. However, since such concentrations were not measured during 2018, further monitoring at this particular site is required to confirm this.

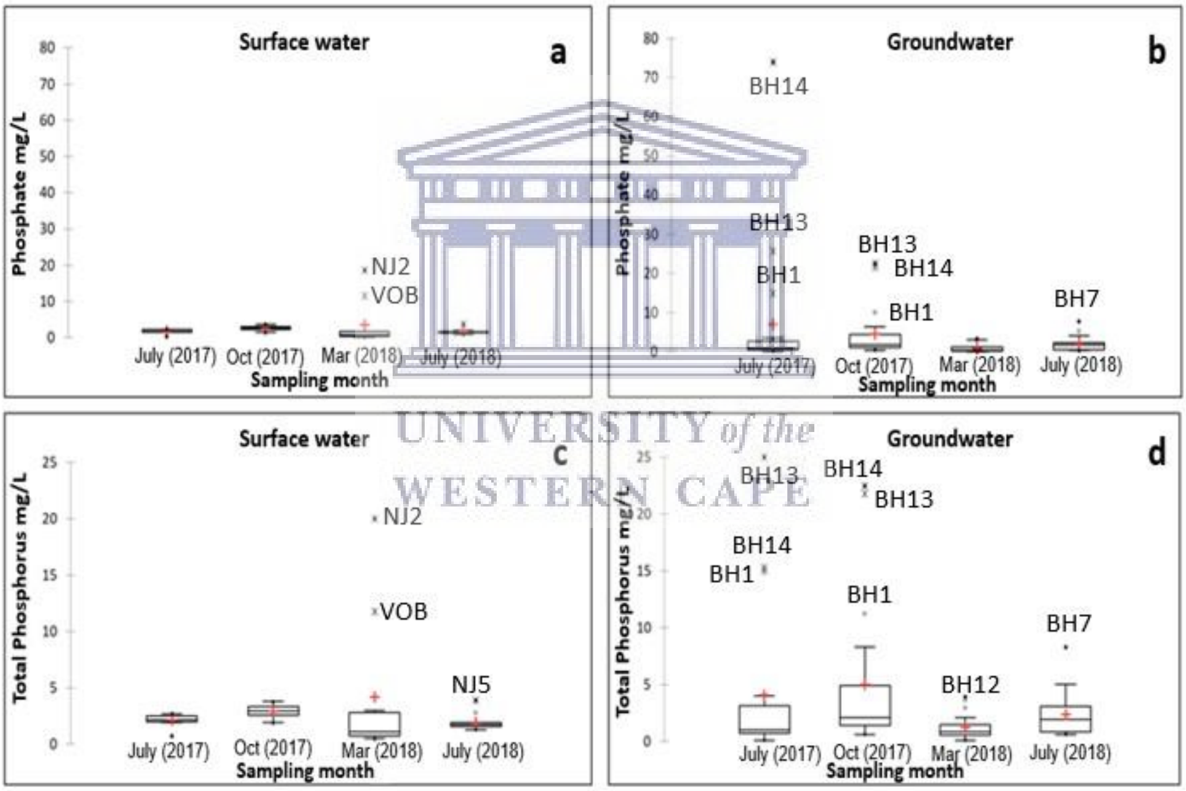


Figure 20: Boxplots of phosphate and total phosphorus in surface water (n= 10) and groundwater (n=20) during the study period.

5.2.7 Suitability of surface and ground water for multiple uses

The South African Water Quality Guidelines, provide specifications and information that can be used to judge the fitness of water for a particular use. To maintain and protect water resources, the aim is to ensure that concentrations of each constitute of water, remain in the No Effect Range, a range that results in no adverse effects, for its intended use. This target is referred to as the Target Water Quality Range (TWQR) (DWAF, 1996). More recently, The

South African National Standard (SANS) 241:2011 provide specifications for acceptable drinking water quality standards. In this section, concentrations of water quality parameters measured in groundwater and surface water are compared to the specifications provided by these guidelines.

5.2.7.1 Domestic Use

The results obtained during the study period indicate that, groundwater in the lower sections of the catchment is not suitable for domestic use. Water quality parameters measured in groundwater in the lower regions of the catchment, with the exception of nutrients and potassium, surpassed the specified TWQR for domestic use, stipulated for each parameter. The results discussed in previous sections also suggest that, groundwater in the uplands of the catchment is generally fresh and of a good quality, consisting of concentrations that fall within the limits specified by the water quality guidelines. Surface waters in tributaries of the Nuwejaars River can be deemed suitable for domestic use, while downstream river waters cannot. Surface water downstream measured EC, chloride, sodium and magnesium concentrations above the TWQR specified for domestic use. Due to high salinities, the majority of groundwater and surface water in the Nuwejaars Catchment does not comply with the drinking water quality guidelines stipulated in the SANS 241 document.

5.2.7.2 Agricultural Use

Sodium and chloride give a direct indication of salinity in water but unlike sodium, chloride in particular is not toxic to crops. Elevated sodium concentrations in irrigation water can be hazardous to crops, and may affect crop yield, crop quality, infiltration rates and hydraulic conductivity in soils. The sodium Adsorption ratio (SAR) is an index calculated to determine the suitability of water for the irrigations of crops. A direct relationship between SAR and EC exists, therefore SAR increases with increasing EC (DWAF, 1996). SAR is calculated based on concentrations of sodium, calcium and magnesium, in irrigation water. This ratio is expressed as:

$$SAR = Sodium / (Calcium + Magnesium)*0.5 \qquad (5.1)$$

The tolerance of sodium in crops varies based on crop type. The stipulated TWQR of SAR for crop yield and quality should not exceed a value of 2. This range ensures that sodium toxicity does not develop in plants sensitive to sodium after irrigation (DWAF, 1996) Crops such as fruits, nuts and citrus, that are sensitive to salinity, require irrigation water with a SAR value between 2 and 8, while more moderately tolerant crops such as clover, oats and rice can withstand higher SAR values of up to 46. Crops such as wheat, barley and tomatoes are tolerant to high sodium concentrations and can be irrigated by water with a SAR value between 46 and 102 without affecting crop quality or crop yield (ANZECC, 2000).

All waters in the Nuwejaars catchment had a SAR value that exceeds 2 (see Appendix 4), primarily due to the high sodium content in waters of the Nuwejaars Catchment. SAR values in groundwater and surface water ranged between a minimum of 2.7 and a maximum of 242 during the sampling period. Although the SAR value from a few sites within the catchment ranged between 2 and 15, the majority of samples yielded SAR values well above 15 but usually below 102. The results indicate that, the majority of waters within the catchment have a high sodium content that can affect sodium-sensitive crops. Crops such as wheat, barley and canola that can tolerate high salinity levels in irrigation water are produced within the catchment. The production of these crops can be attributed to the quality of water available for irrigation within the catchment.

Concentrations for water quality parameters measured in groundwater and surface water during the study period indicate that the majority of waters in the Nuwejaars Catchment are generally suitable for livestock production, particularly for livestock produced within the catchment (sheep and cattle). Downstream waters, however, recorded chloride and sodium concentrations above the TWQR of 0 – 100 mg/L for both constitutes. Although some livestock may be able to tolerate and adapt to increased concentrations of some constitutes, this is depended on factors such as the duration of exposure to waters with elevated concentrations (DWAF, 1996).

5.2.7.3 Implications of using water quality guidelines as a reference for N-PRs

The South African Water Quality Guidelines (SAWQG) are a reference stipulated for water resources under normal conditions, and do not necessarily adequately represent naturally variable systems such as N-PRs that differ significantly from permanent rivers. As a result, a water quality parameters measured during the current study, did not adhere to the specifications provided by these guidelines, especially in lower regions of the catchment. Although it is common practice to assess the quality of water resources based on these guidelines, it may not be practical for such complex systems. Previous studies by Rossouw et al. (2005) and Von Schiller et al. (2011) emphasised that reference conditions used to evaluate the chemical status of permanent rivers may not be suitable to evaluate the chemical status of temporary rivers and that the use of such criteria on N-PRs may provide inaccurate and misleading findings. The consideration of this aspect is therefore necessary when conducting water quality investigations in such systems.

5.2.8 Multivariate Statistics

To further characterise groundwater and surface water, multivariate statistical methods, Cluster Analysis and Principle Component Analysis, were conducted to identify groups of samples with similar chemical compositions. Information on the statistical methods and the procedure of the analysis were previously discussed in the data analysis section of the methods chapter. The statistical analysis was based on the variables assessed during this study (temperature, EC, pH, calcium, sodium, potassium, magnesium, chloride, sulphate, bicarbonate, total nitrogen and total phosphorus). The output of hierarchical Cluster Analysis (CA) is a dendrogram that shows clusters or groups of similar samples (see Figure 21) while Principle Component Analysis (PCA) generates factor loadings, eigenvalues, cumulative percentages of variance and the overall PCA plot (Figure 23).

5.2.8.1 Cluster Analysis

The dendrogram generated (Figure 21), consists of 5 distinctive groups of clusters; these clusters are also illustrated on the PCA plot (Figure 23). Samples in each group represent waters with a similar chemical compositions.

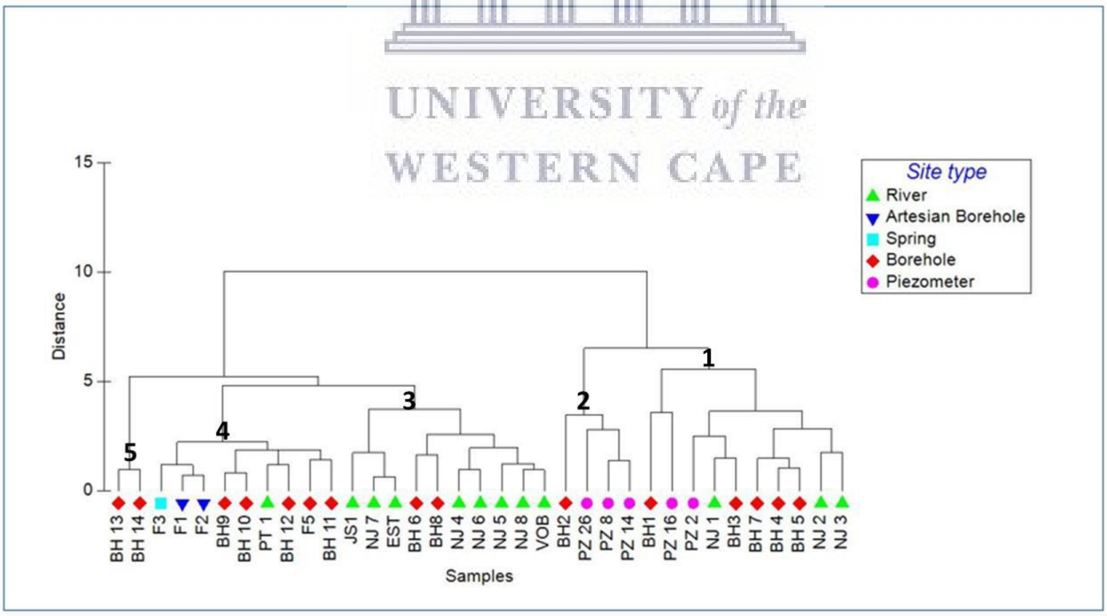


Figure 21: Cluster analysis results of groundwater and surface water in the Nuwejaars Catchment.

Cluster 1 consists of a total of 10 samples, collected from, river, deep groundwater and shallow groundwater sites, NJ1, NJ2, NJ3, BH1, BH3, BH4, BH5, BH7, PZ 2 and PZ16. The majority of these samples were collected in the lower sections of the catchment, with the exception of BH4, BH5 and BH7, which were collected towards the middle sections of the catchment. No samples from the upper sections of the catchment, before the town of Elim fell within this group (see Figure 21). Samples NJ1, NJ2 and NJ3 are from river sites, located at the far end of the catchment, closest to the coast. BH 1 and PZ16, which are very similar, despite their differences in depth, are both located at SANparks. Cluster 1, consists of samples with the second highest salinity concentrations. Samples within this cluster are characterised by high chloride and sodium concentrations and therefore high EC Values. The clustering of surface water and groundwater samples, gives an indication of waters that are influenced by the same hydrological processes.

Cluster 2 consists of a total of 5 samples (PZ26, PZ8, PZ14, and BH2)**,** collected mostly from shallow groundwater. This cluster, consists of samples with the highest salinities. Similarities in chemical composition of samples within this cluster could possibly be attributed to similarities in depths at which the samples were collected. These samples were also collected at sites within close proximity to each other, mostly downstream.

Cluster 3 consists of a total of 10 samples, mainly river samples. Samples included within this cluster are NJ4, NJ5, NJ6, NJ7, NJ8, VOB, JSI, ETS, BH6, and BH8. Geographically, these samples were collected in the mid to upper sections of the catchment. The most similar samples within this cluster were collected geographically in close proximity to each other, therefore similarities in surface waters could be attributed to similar vegetation, geology types and overall surrounding human activities. Although not the group with the lowest salinities, these sites are characterised by moderate to low salinity levels and two of the freshest river samples (JSI and ETS) are within this cluster. The large number of river sample within this cluster suggest that river samples are more similar to each other as compared to groundwater, in terms of their chemical composition.

Cluster 4 consists of 9 samples, primarily collected from deep groundwater. These samples were collected upstream of the catchment at high altitudes, furthest from the coast. These include, BH12, BH11, BH10, BH9, F1, F2, F3, F5 and PT1. These samples are characterized by low salinities and are generally fresh. The low mineral content of these samples can be attributed to the weathered and fractured sandstone layers that underlie the upper sections of the catchment. This type of geological formation is weathered and therefore, very low in salts (Diamond, 2014). The only river sample within this cluster, PT1 has a similar chemical composition to groundwater because, according to Mazvimavi (2017) tributaries of the Nuwejaars River are fed by constant base flow from deep ground systems.

Cluster 5 consists of only 2 samples, BH13 and BH14, located upstream at Uitsig farm near the town of Elim (see Figure 7 and 22). Waters in this group are characterized by low salinities. Similarly to cluster 4, low salinity concentrations in this group can be attributed to the geology type (weathered sandstones), that dominates in the upper sections of the catchment.

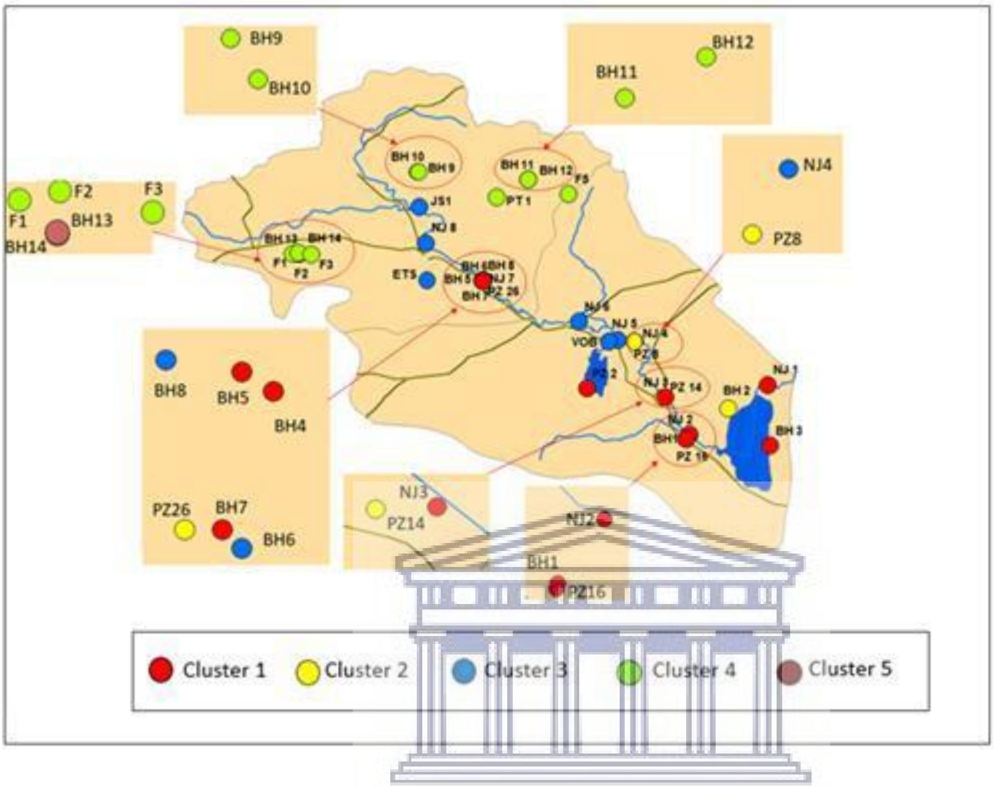


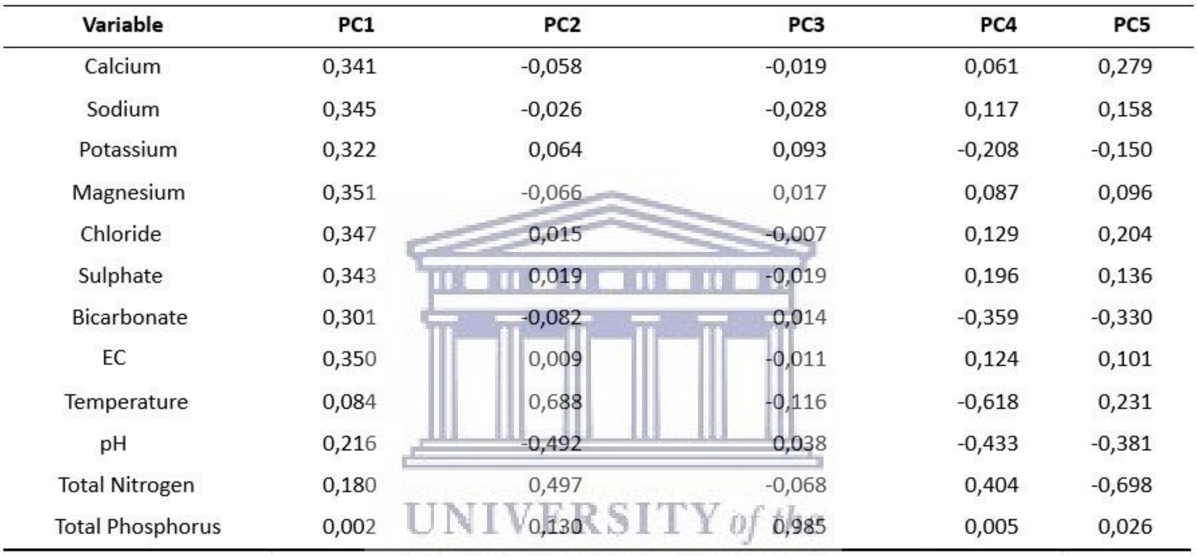
Figure 22: Geographical location of surface water and groundwater sampling sites, categorized into clusters.

5.2.8.2 Principle component analysis

The Principle component analysis (PCA) conducted, included a total of 12 variables, measured in groundwater and surface water of the Nuwejaars Catchment. The results generated from the PCA which include the eigenvalues, and cumulative percentage of variance for each of the extracted components are presented in Table 9.

Table 9: Principle component analysis results: eigen values and percentage variations

PC	Eigenvalues	%Variation	Cum.%Variation
1	7,87	65,6	65,6
2	1,26	10,5	76,1
3	1,01	8,4	84,5
4	0,743	6,2	90,7
5	0,606	5,1	95,7



Variable	PC1	PC2	PC3	PC4	PC5
Calcium	0,341	-0,058	-0,019	0,061	0,279
Sodium	0,345	-0,026	-0,028	0,117	0,158
Potassium	0,322	0,064	0,093	-0,208	-0,150
Magnesium	0,351	-0,066	0,017	0,087	0,096
Chloride	0,347	0,015	-0,007	0,129	0,204
Sulphate	0,343	0,019	-0,019	0,196	0,136
Bicarbonate	0,301	-0,082	0,014	-0,359	-0,330
EC	0,350	0,009	-0,011	0,124	0,101
Temperature	0,084	0,688	-0,116	-0,618	0,231
pH	0,216	-0,492	0,038	-0,433	-0,381
Total Nitrogen	0,180	0,497	-0,068	0,404	-0,698
Total Phosphorus	0,002	0,130	0,985	0,005	0,026

The PCA produced five principle components (Table 9), although interpretation here is limited to the first two (PC1 and PC2) which account for the largest percentage variance. According to Kaiser (1960) and Madlala (2015), only components with eigenvalues above 1 that are responsible for the largest percentage of variation should be interpreted. PC1 and PC2 collectively accounted for a total percentage variance of 76.1 %. PC1, which accounted for 65.6 percentage variance with an eigenvalue of 7.87, is correlated with all the parameters included in the analysis.

In PC1, although all below a loading of 0.5, values of chloride, sodium, EC, calcium, magnesium and sulphate, yielded similar loadings. Positive loadings for chloride, sodium and EC, which are indicators of salinity, suggest the influence of rock-to-water interactions on waters within the catchment (Madlala 2015; Laar, 2018), processes that will be further discussed in sections to follow. Positive loadings for sulphate indicate influences from surrounding land uses, on water chemistry, while lower loadings for TP and TN indicate influences of agricultural activities on water chemistry, although to a lesser extent. Values for calcium and magnesium give an indication that the dissolution of carbonates influences the chemistry of waters within the catchment (Laar, 2018). PC2, which accounted for a percentage variance of 10.5 with an eigenvalue of 1.26, also yielded large positive loadings for, total nitrogen and total phosphorus. This also gives an indication that land-use activities influence water quality. The results generated from PC1 and PC2 are indicative of influences of natural processes such as water-rock interactions and human activities on water quality within the Nuwejaars Catchment. Unlike in this section, the results obtained in previous sections do not give an indication that land-uses within the catchment influence water quality. Further investigations on the influence of land-use on water quality are required, since some results show a possibility that they may influence water chemistry, while other results do not.

The results from the PCA are presented in Figure 23. Groundwater and surface water sites were grouped into their respective clusters. From Figure 23, it is evident that clusters 1 and 2 are representative of the most saline waters, consisting of the highest concentrations of major ions and EC, while clusters 4 and 5 represent the freshest waters within the catchment.

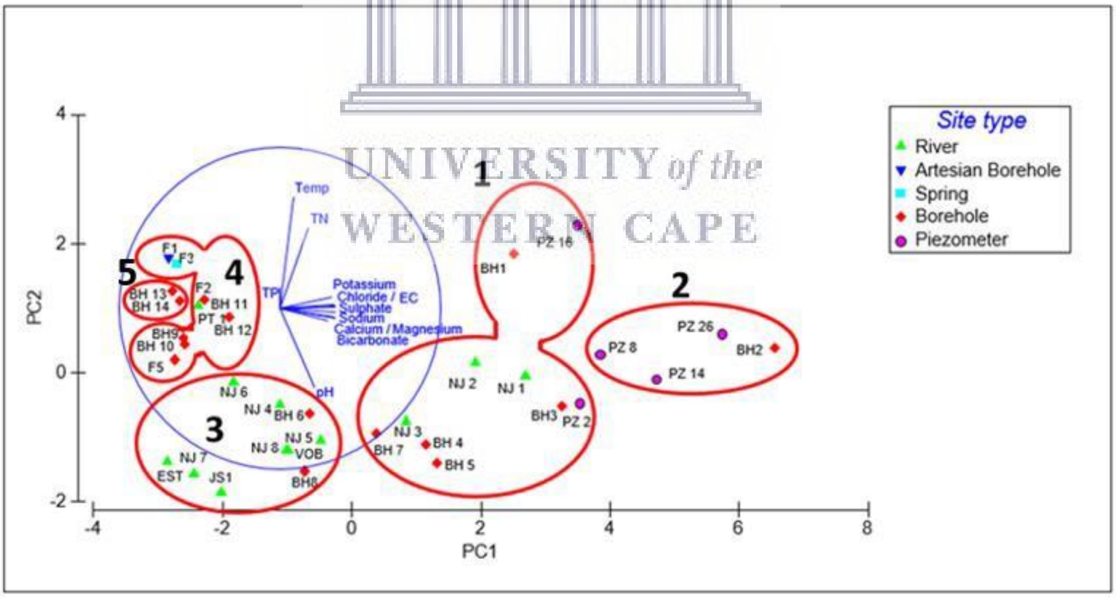


Figure 23: PCA plot of physico-chemical variables of groundwater and surface water in the Nuwejaars Catchment.

5.3 Determination of hydrogeochemical processes

5.3.1 Characterization of water type

Water type was characterized using Piper diagrams (Piper 1944). Piper diagrams in this section have also been applied to gain insight on the chemical evolution or origin of groundwater in the Nuwejaars Catchment. The ionic proportions, expressed in meq/L, of groundwater and surface water in the Nuwejaars Catchment are presented in Figures 24-27.

Results indicate that groundwater and surface water in the Nuwejaars Catchment is confined to the sodium-chloride type (Na-Cl type) and these are therefore the dominant ions in all waters within the catchment. Calcium, magnesium, potassium and bicarbonate were present in less significant amounts. The piper diagrams do not give an indication of recently recharged or fresh groundwater within the Nuwejaars Catchment. Instead, the piper diagram gives an indication of a costal aquifer, consisting of deep ancient groundwater that is expected to be saline. According to Panno et al. (2002) and Nonterah (2015), groundwater of an Na-Cl water type reflects a strong seawater influence giving an indication of a costal aquifer that is in close proximity to the sea. This can be validated by the short distance between the sea and groundwater sampling locations within the catchment. In a previous study that focused on the chemistry of groundwater and surface water in a costal environment, of the Sakumo Wetland in Ghana, Nonterah et al. (2015) also reported on the confinment of water samples in the Na- Cl water type region of the piper diagram.

The dominance of sodium and chloride ions in groundwater in the lower topographic regions of the catchment, characterized by low elevations (5m), can be attributed to the process of mineralization. Low hydraulic gradients downstream limits groundwater flow, resulting in slow moving groundwater with a long residence time (Kumar et al., 2016). This process favours rock-water interactions and is responsible for the presence of mineralized or saline groundwater in the lower topographic regions of the catchment. According to Kumar et al. (2016) the dominance of sodium and chloride ions also suggests that the process of evaporation is prominent within the study area.

No temporal changes in water type were observed during the study period (Figures 24-27), however some variations in the abundance of ions can be observed. According to Major et al. (2013), the lack of temporal changes in water type suggests ionic stability in waters. Similarities in water type observed in groundwater and surface water give an indication of waters that originates from the same or a similar source. This also suggests that similar hydrogeochemical process influence the chemistry of both water sources within the catchment (Manoj et al., 2013; Gxokwe, 2017).

The piper diagram generated for July 2017 during the wet season shows 2 samples (PZ19 and BH10) that plotted separately from the rest the cluster of samples (Figure 24). PZ19 plotted near the mixed water region, which implies that sodium and chloride were not as dominant, instead ions were present in almost equal proportions in this particular sample. Due to gaps that exist within the data set, major ion compositions measured for PZ19 were recoded only for July 2017, therefore a constant pattern that shows differences in the ionic proportions between this sample and the rest of the cluster could not be established. However, it is likely that PZ19 plots separately because the chemistry of shallow groundwater at that site is affected by the clay and peat material within the subsurface zone, where the samples were collected. In addition the calcrete limestones within the location of PZ19 undergo evaporative processes that can potentially affect the water quality of this sample. In BH10, the dominance of calcium and magnesium was slightly more pronounced as compared to the rest of the samples, this is typical of groundwater in mountainous regions. During the onset of the dry season (October 2017), no obvious outliers were observed.

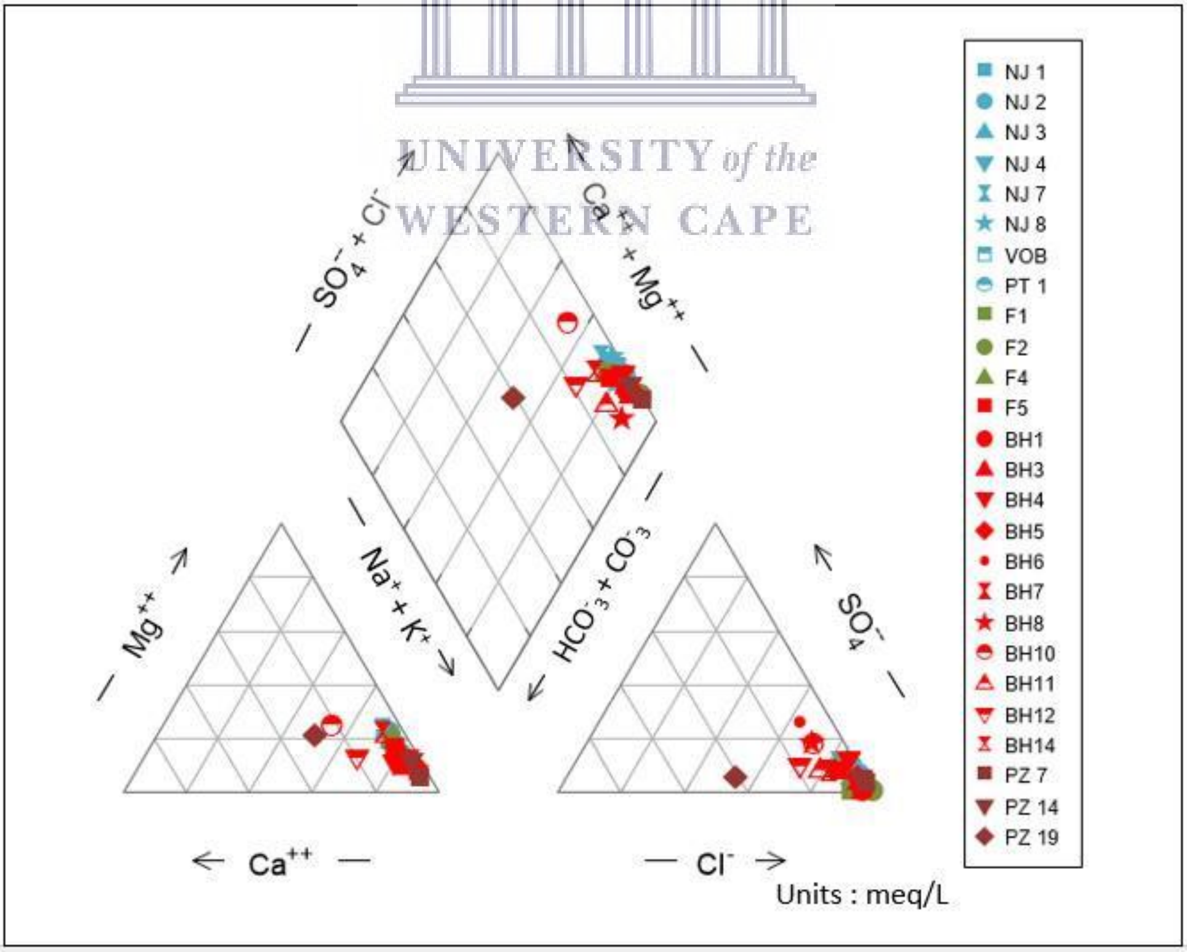


Figure 24: Piper diagram of groundwater and surface water, July 2017 (wet season).

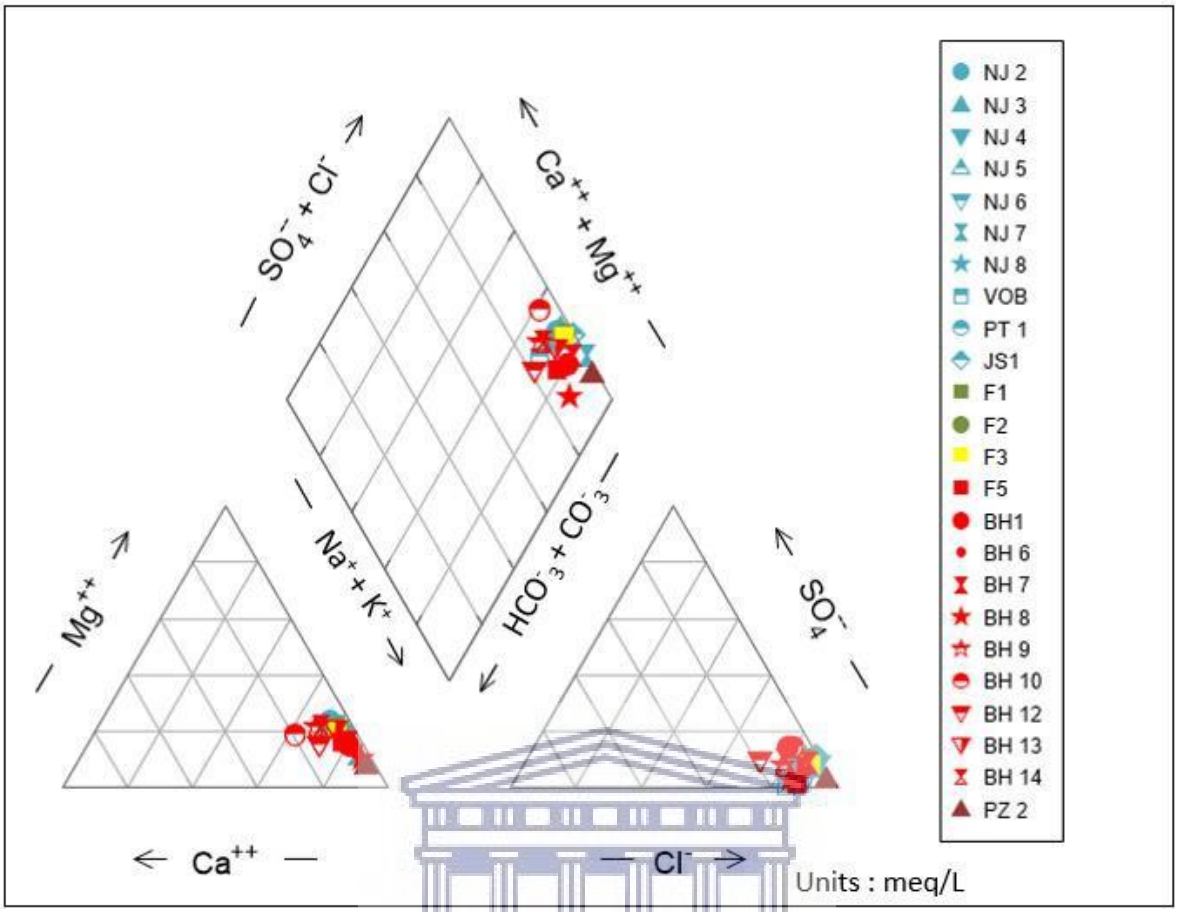


Figure 25: Piper diagram of groundwater and surface water, October 2017 (onset of dry season).

Figures 26 and 27 show a slight separation in the clustering of groundwater and surface water, a separation that was previously not evident in 2017. Groundwater flow within the catchment is controlled by the recharge areas underlain by TMG formations and existing fault systems. The chemical composition of groundwater is therefore also influenced by groundwater of a different nature entering the system from other catchments. This process may be responsible for the slight variations in ionic proportions observed between groundwater and surface water during these seasons.

Although useful in categorizing samples based on their relative proportions of major ions, piper diagrams do not show variations in the ionic composition of samples. As a result, dilute and saline samples may plot within the same region. This is evident from piper diagrams generated for waters of the Nuwejaars Catchment. Fresh samples from groundwater in the uplands plots together with saline groundwater downstream.

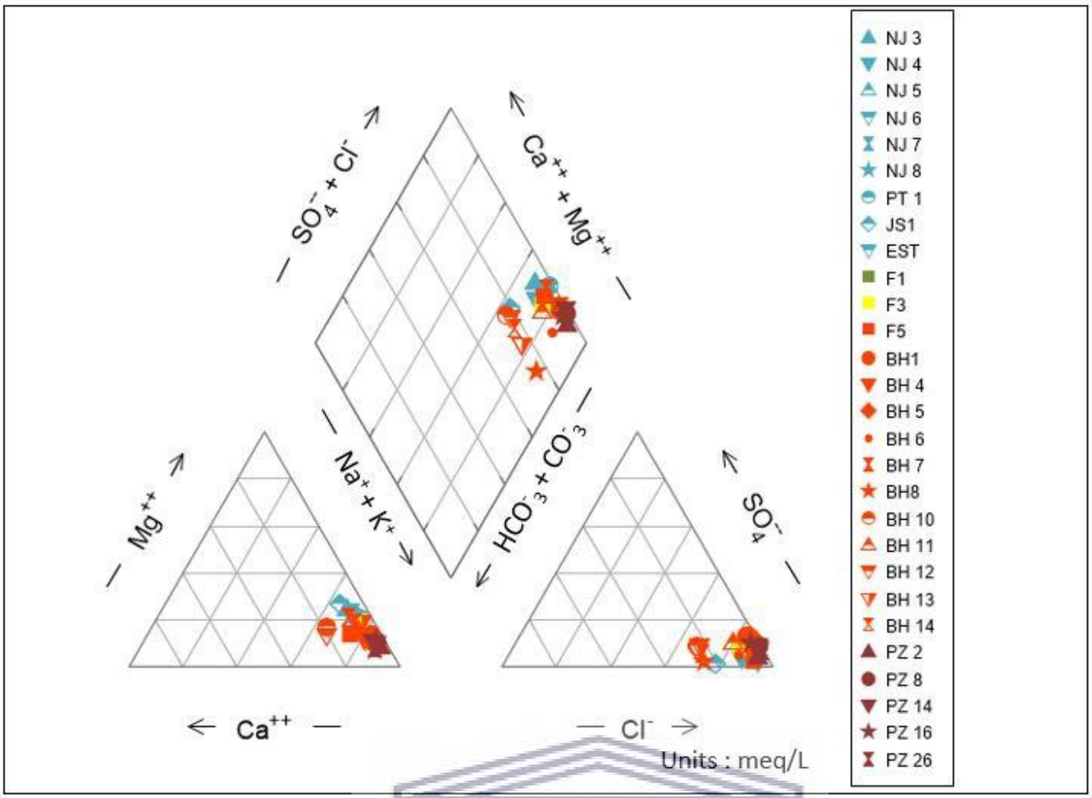


Figure 26: Piper diagram of groundwater and surface water, March 2018(dry season).

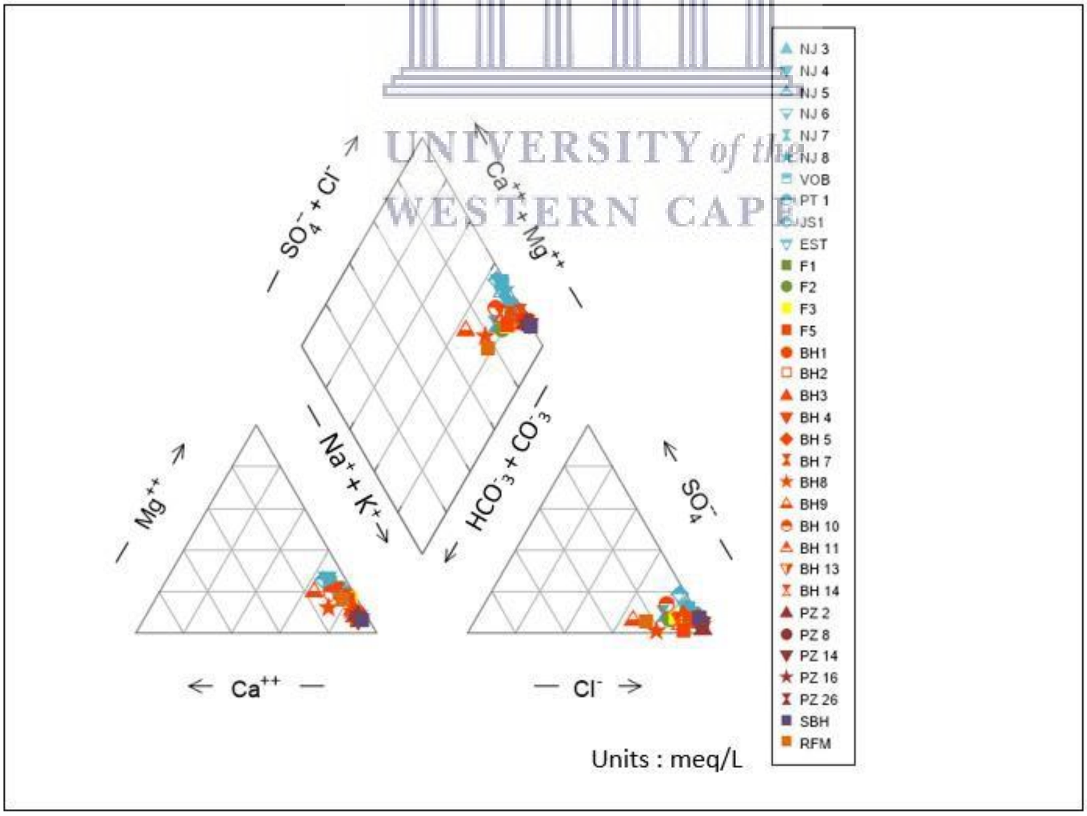
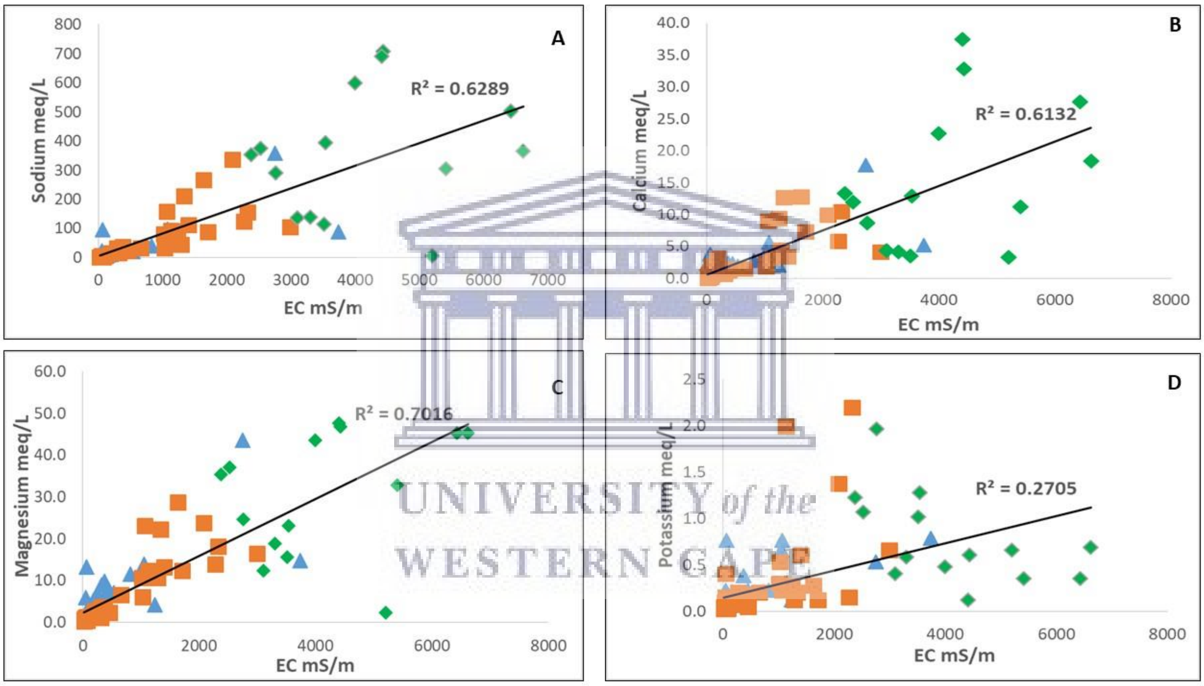


Figure 27: Piper diagram of groundwater and surface water, July 2018 (Wet season).

5.3.2 Sources of salinity in the Nuwejaars Catchment

To identify the ions responsible for salinity within the catchment, scatter plots illustrating the relationship between EC and major ions were generated. According to Solomon (2013) and Laar (2018) the relationship between EC and major ions can be used to determine sources or contributors of salinity that influence water chemistry in a catchment. The relationship between EC and major ions is presented in Figure 28. The generated scatter plots give an indication of the extent to which each ion contributed to salinity in waters of the Nuwejaars Catchment. A correlation coefficient (R^2) above 0.7 is considered as a strong correlation, while a correlation coefficient between 0.5 and 0.7 is considered as a moderate correlation (Venkatramanan et al., 2013; Laar, 2018).



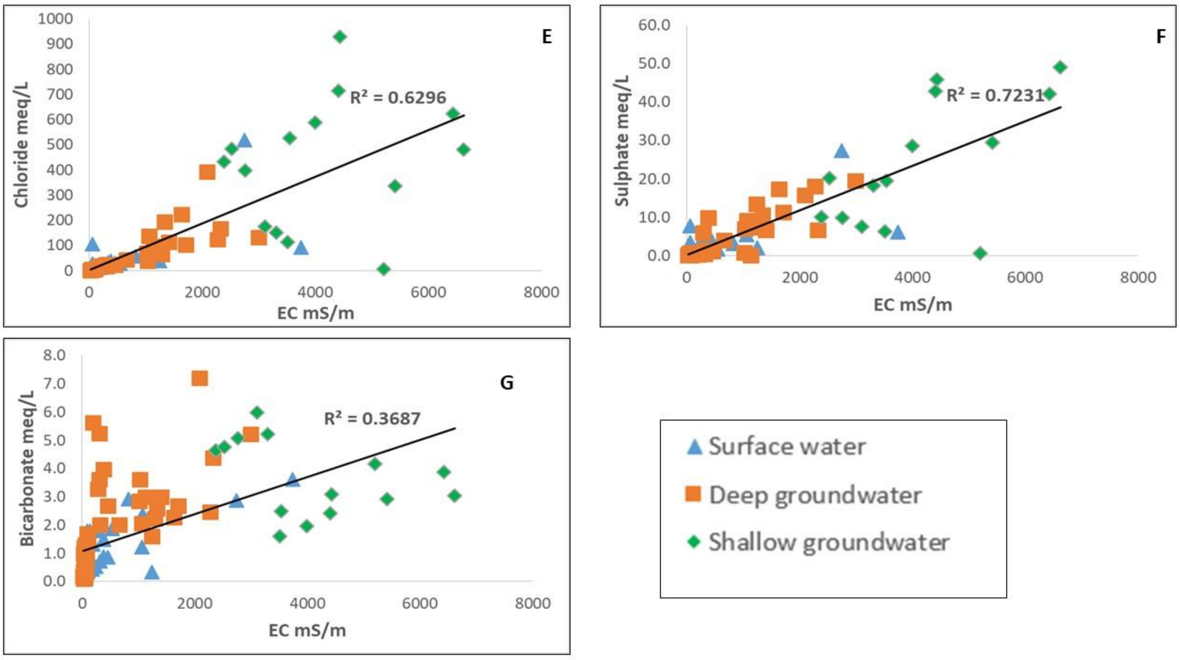


Figure 28: The relationship between electric conductivity (EC) and major ions of groundwater and surface water (n= 103).

Groundwater and surface water in the Nuwejaars Catchment in previous sections, has been characterized as belonging to the Na-Cl water type. It was therefore expected that the relationship between chloride and sodium with EC would compute the highest correlation coefficients. According to Peinado-Guevara et al. (2012), chloride ions are the main constitute of water that affects EC, hence a number of studies (Oteri, 1988; Xu and Eckstein, 1997) found the a strong correlation between chloride and EC. The results generated indicate that, sulphate, magnesium, sodium, chloride and calcium all contribute to salinity in appreciable amounts, with R^2 values ranging between 0.6 and 0.72, representing moderate-high correlations with EC. This is despite the fact that concentrations recorded for sulphate, magnesium and calcium were not as abundant as those recorded for sodium and chloride in waters of the Nuwejaars Catchment. The results obtained, indicate the possibility of a combination of processes influencing water chemistry to similar extents within the catchment, however further research is required to confirm this.

The computed correlation coefficient of sodium and chloride with EC indicates, the leaching of rock minerals, and the influence of sea sprays on water quality (Venkatramanan et al., 2013). On the other hand, results obtained for relationships between EC and magnesium, sulphate and calcium suggest a contribution of salinity from silicate and carbonate weathering from rocks such as limestones, which are present in sections of the study area. The results generated from the correlation plots, that did not produce the strongest correlations between EC with chloride or sodium, did not correspond with the order of abundance of concentrations recorded in Table 7, or from findings deduced from the piper diagrams, that explicitly identified sodium and chloride as the dominant ions in all waters, thus the primary contributors of salinity. Furthermore, the relationship between potassium and bicarbonate with EC, computed the lowest correlation coefficients of 0.27 and 0.37 respectively. Potassium and bicarbonate therefore have a low correlation with EC, which suggests that they contribute the least towards salinity in waters of the catchment (Laar, 2018).

According to Solomon (2013) and Venkatramanan et al. (2013), the computed R^2 values provide the proportion of the variability of the dependent variable in correlation analysis. The computed R^2 values for sulphate, magnesium, sodium, chloride and calcium suggest that 61-72% of the variability of the dependent variables were accounted for by the analysis. The remaining 28-39% of factors that were unaccounted for indicate the percentage of unknown variability of the dependent variable (Lambing, 1983; Solomon, 2013). The correlation analysis explains a good proportion of the variability of major ions with respect to their relationship with EC. On the contrary, R^2 values computed for the relationship between potassium and bicarbonate with EC, indicate that 76% of the variability for potassium and 63% of the variability for bicarbonate were unaccounted for by the analysis. A large proportion of the variability of the dependent variable (potassium and bicarbonate concentrations) cannot be explained by the correlation analysis.

5.3.3 Hydrogeochemical processes influencing groundwater chemistry

To identify hydrogeochemical processes that influence groundwater chemistry in the Nuwejaars Catchment, bivariate correlation plots and stoichiometric analysis were applied as identification tools. The combined use of these tools allows for a comprehensive assessment of relationships between ions. The correlation coefficient values obtained from the bivariate correlation plots were used to establish the strength of each relationship. The computed R^2 values in Figure 29 with the exception of Figure 29b, indicate that the correlation analysis accounts for more than 80% of the variability of the dependent variables, providing good results. The relationships between major ions are presented in Figure 29.

The relationship between Na^+ and Cl^- illustrated in Figure 29a, indicates a positive correlation between the two ions, suggesting that they originate from the same source. The source of these ions in groundwater are likely to be as a result of the leaching of evaporates into the subsurface or the infiltration of precipitation of a sodium-chloride type. The relationship between these two ions is usually assessed to identify the influence of halite dissolution (Hem, 1985). However, although the results are consistent with those expected to indicate the dissolution of halite as a geochemical process affecting groundwater quality, there is no evidence that halite is present within the study area.

To identify evaporation as a major process influencing groundwater chemistry, the relationship between the Na/Cl ratio and EC can be assessed (Saini et al., 2016; Laar, 2018). The Na/Cl versus EC scatter plot generated for groundwater of the Nuwejaars Catchment yielded a correlation coefficient of 0.03, suggesting a weak non-linear correlation. Jankowski and Acworth (1997) and Saini et al. (2016), explained how the process of evaporation causes EC concentrations to increase, while the Na/Cl ratio remains constant. Figure 29b shows that the Na/Cl ratio remained constant with an increase in EC. The results therefore indicate that, evaporation does influence groundwater chemistry in the study area. This was expected since evaporation is usually dominant in arid and semi-arid regions.

Processes of ion exchange, reverse ion exchange and the weathering of minerals in groundwater can be assessed using the relationship between (Ca^{2+} +Mg^{2+}) and (HCO_3^{-} + SO_4^{2-}). Elango and Kannan (2007) and Laar (2018) explained that, groundwater samples that fall above the 1:1 line are influenced by the dissolution of carbonate minerals, whereas samples that fall below the 1:1 line are influenced by the dissolution of silicate minerals. Furthermore, Kumar et al. (2016) and Ligavha-Mbelengwa (2017), stated that, groundwater samples that plot above the 1:1 line indicate the presence of reverse ion exchange, while those that fall below the 1:1 are influenced by ion exchange. Figure 29c, shows a fair amount of samples both below and above the 1:1 line, this suggests that ion exchange, reverse ion exchange, carbonate and silicate weathering all influence groundwater chemistry in the catchment to some extent. The majority of shallow groundwater plotted above the line, suggesting that piezometric waters are mostly influenced by reverse ion exchange and carbonate weathering. These samples lie within the limestone region where these processes are common.

To confirm the influence of ion exchange and the weathering of carbonates and silicates in groundwater, the ratio proposed by Hounslow (1995) was applied. Calcium and sulphate concentrations of groundwater in meq/L, were substituted into the following expression;

$$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}} \qquad (5.2)$$

The ratios calculated for groundwater from the expression above are presented in Appendix 6. The majority of the samples (65%), computed a ratio less than 0.5. According to, Hounslow (1995) and Ligavha-Mbelengwa (2017) who also applied the same tools for groundwater characterization, a ratio of < 0.5 coupled with a pH of < 5.5 indicates pyrite oxidation, while a ratio < 0.5 with a neutral pH would suggest that ion exchange or calcite precipitation are the sources of calcium and sulphate in groundwater. On the other hand, a ratio > 0.5 indicates that sources of calcium may be from carbonates and silicates. Groundwater in the Nuwejaars Catchment was previously characterised as having a pH below 7 in deep groundwater but above a pH of 5.5 in most cases and between 7 and 8 in shallow groundwater. Based on this information it can be deduced that pyrite oxidation does not influence the chemistry of groundwater, instead calcium ions in groundwater of the Nuwejaars Catchment are primarily derived from ion exchange and from carbonates and silicates to a lesser extent.

To verify the occurrence of ion exchange and reverse ion exchange, the following expression proposed by Hounslow (1995) was applied;

$$\frac{Na^+}{Na^+ + Cl^-} \tag{5.3}$$

Sodium and chloride concentrations in meq/L were substituted into the expression. The ratios calculated from this expression are presented in appendix 6. The calculated ratios were close to 0.5 or below 0.5 in most cases. According to, Hounslow (1995), if the ratio is less than 0.5 and the TDS is greater 500 mg/l, it is an indication of water from brines or connate sources, where reverse ion exchange has occurred. The results therefore, indicate that groundwater in the Nuwejaars Catchment is influenced by connate sources of water that experienced reverse ion exchange.

The calcium versus Sulphate correlation plot computed an R^2 value of 0.82, showing a strong positive correlation between the two ions. The results from this analysis explain over 80% of the variability of the dependent variable. Figure 29d, shows that a fair number of groundwater samples did not plot along the 1:1 line. According to Jalali (2007) and Ligavha-Mbelengwa (2017), this indicates that gypsum dissolution is not the main source of calcium ions in groundwater. The ratio of Mg/Ca indicated that the majority of groundwater within the Nuwejaars Catchment is influenced by calcite dissolution since ratios above 1 were computed. According to Mayo and Loucks (1995) and Ligavha-Mbelengwa (2017) the dissolution of pure dolomite in groundwater is represented by a Mg/Ca ratio of 1, while a ratio greater than 1 indicates calcite dissolution.

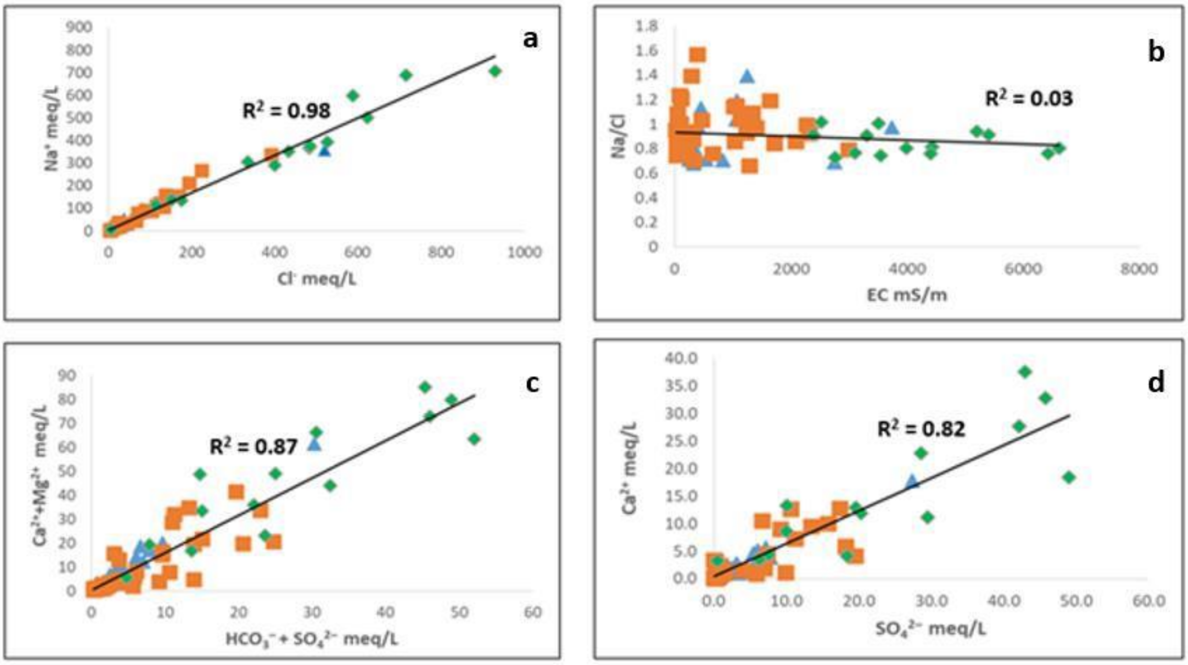


Figure 29: The relationship between major ions in groundwater (n= 64).

5.4 Establishing interactions between groundwater and surface water

This section reports on findings from the stable isotope analysis. Isotopes of the water molecule oxygen-18 also denoted as δ^{18}O and deuterium denoted as δ^{2}H were analysed in waters of the Nuwejaars Catchment during the dry and wet season of 2018. In this section, environmental isotopes were used as confirmatory tools to establish interactions between groundwater and surface water. Isotope compositions of groundwater and surface water and the positions at which they plot relative to the local meteoric water line (LMWL) and global meteoric water line (GMWL) during the wet and dry season are described. This description assists in identifying similarities and differences in isotope signatures of groundwater and surface water, which allows for interactions between the two sources to be established. The information below, provides a statistical summary of the data, detailed results are presented in Appendix 5. Results from the significance tests reported on in this section are presented in Appendix 7.

Table 10: Statistical summary of isotope compositions of groundwater and surface water.

a) Surface Water

	March 2018 (Dry season)			July 2018 (Wet season)		
	δ^{2}H, in ‰	δ^{18}O, in ‰	d -excess	δ^{2}H, in ‰	δ^{18}O, in ‰	d –excess
Min	-22.9	-5.12	-18.64	-21.1	-4.92	-0.08
Max	38.8	7.08	18.06	9	0.92	18.7
Mean	12.87	1.8	-1.51	-6.79	-2.1	9.98

b) Groundwater

	March 2018 (Dry season)			**July 2018 (Wet season)**		
	δ^{2}H, in ‰	δ^{18}O, in ‰	d -excess	δ2H, in ‰	δ18O, in ‰	d –excess
Min	-24	-5.48	7.1	-24.5	-4.76	2.94
Max	-5.9	-1.7	22.86	-8.9	-2.2	18.64
Mean	-16.47	-3.72	13.31	-17.23	-3.55	11.2

Results from the isotopic analysis conducted for waters of the Nuwejaars Catchment during March and July 2018 are presented in Table 10. During the dry season (March 2018), δ^{2}H and δ^{18}O compositions in groundwater ranged between -24 and -5.9 ‰, with a mean of -16.47‰ for δ^{2}H and -5.48 to -1.7 ‰, with a mean of -3.72 ‰, for δ^{18}O. In surface water the isotope compositions of δ^{2}H ranged between -22.9 and 38.8 ‰, while, δ^{18}O values ranged between -5.12 and 7.08 ‰ during the dry season. From Figure 30, it is evident that groundwater samples that plotted in the lower left quadrant of the plot were more depleted, as they yielded negative δ^{2}H and δ^{18}O values. Positive δ^{2}H and δ^{18}O values were measured for surface water, suggesting that those samples were enriched (Gxokwe, 2017).

The results obtained from the stable isotope analysis for samples collected during the wet season (July 2018) are represented in Figure 31. In groundwater, δ^2H and δ^{18}O compositions ranged between -24.5 to -8.9 ‰ and -4.76 to -2.2 ‰ respectively. In surface water the isotope ratios of δ^2H ranged between -21.1 to 9‰, meanwhile, δ^{18}O values ranged between -4.92 to 0.92 ‰ during this season. The rainfall sample plotted the furthest away from the 0‰ of VSMOW (Vienna Standard Mean Ocean Water), with a composition similar to groundwater samples collected in the upper catchment. The d-excess value of groundwater during the dry season had a mean of 13.31 and ranged from 7.1 to 22.86. During the wet season the d-excess value of groundwater ranged between 2.94 and 18.64 with a mean of 11.20, a decrease compared to the dry season.

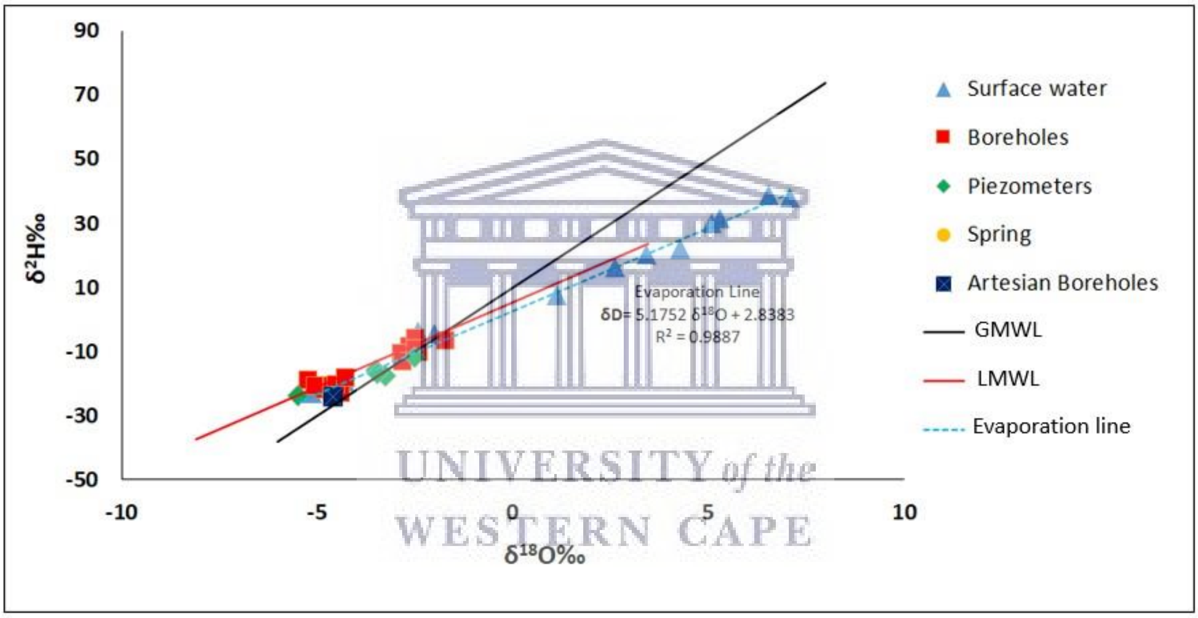


Figure 30: The relationship between δ^2H and δ^{18}O compositions of groundwater and surface water, March 2018 (dry season).

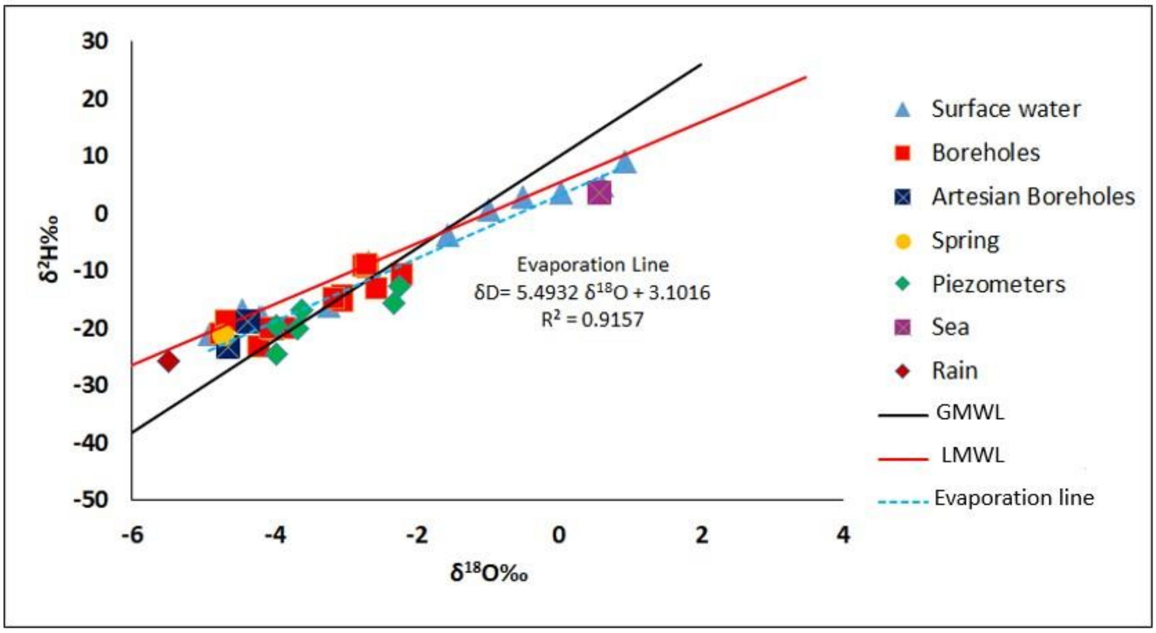


Figure 31: The relationship between δ^2H and δ^{18}O compositions of groundwater and surface water, July 2018 (wet season).

The temporal and spatial variations observed in isotope compositions of groundwater and surface water show evidence of the influence of seasonal, latitude, altitude and continental effects as described in the literature review chapter. A strong relationship between temperature and isotope compositions exists (Clark and Fritz, 1997). High temperatures experienced during summer increase evaporation rates that result in the enrichment of δ^2H and δ^{18}O (Kendall and Coplen, 2001). Surface water is in direct contact with sunlight, and therefore experiences higher evaporation rates as compared to groundwater, hence we generally expect them to plot differently unless an interaction exists. This is evident in Figure 30, showing results from the summer season, where most of the surface water samples were highly enriched and evaporated, forming a linear pattern below the local meteoric water line (LMWL) and global meteoric water line (GMWL), indicating an influence of direct evaporation, while groundwater samples were depleted and clustered between the LMWL and GMWL. On the contrary, as expected, during the wet season (July 2018), the isotope compositions of surface water samples were slightly depleted. This can be attributed to the rainout process driven by decreasing temperatures which result in depleted ^{18}O and ^{2}H compositions (Clark and Fritz, 1997; Gxokwe, 2017).

The dry season showed a larger number of enriched surface water samples (8 out of 12 samples), while in winter this number decreased (2 out of 12), with δ^{18}O values less than 1 ‰ and δ^2H less than10 ‰. Depleted isotope signatures in river samples during the wet season, are expected because, there is a sufficient amount of rainfall with low isotope signatures during this period that alters the isotopic compositions of river waters (Kendall and Coplen 2001;

Gxokwe, 2017). From Figure 30 and 31, it is clear that variations in temperatures due to seasonal differences largely influence the isotopic compositions of surface water, unless an interaction with groundwater is eminent. The influence of seasonality on isotope signatures was not as pronounced in groundwater as previously discussed for surface water. This is generally because seasonal variations in groundwater are minimal. In groundwater, seasonal variations in isotope compositions are lost during infiltration through the unsaturated zone (Clark and Fritz, 1997).

Boreholes and river samples collected upstream of the catchment, at higher elevations, yielded depleted $\delta^{18}O$ and $\delta^{2}H$ compositions, because isotope compositions are known to decrease with an increase in altitude and because temperatures at higher altitudes are generally lower than those at lower altitudes. In addition, $\delta^{18}O$ and $\delta^{2}H$ values decreased with distance inland. Surface water downstream reflects more enriched values as compared to those further inland. In groundwater, isotope compositions from boreholes furthest from the sea exhibited more depleted compositions. Continental effects on isotope compositions result in a decrease in $\delta^{18}O$ and $\delta^{2}H$ values with distance from the sea (Clark and Fritz, 1997; Laar, 2018).

Meteoric and subsurface processes influence ^{18}O and ^{2}H signatures, such that they plot below the LMWL (Clark and Fritz, 1997). This is evident from the plots above, were groundwater plots below the LMWL. Borehole water that plotted closest to the LMWL is indicative of deep groundwater influenced by little to no evaporation e.g. deep artesian boreholes. On the other hand, groundwater that plots near or below the GMWL has been impacted by evaporation (Kendall and Coplen 2001). Groundwater clustered well between the LMWL and the GMWL and was characterised by similar isotope compositions to that of local rainfall. This gives an indication that the primary source of groundwater recharge in the catchment is infiltration from local rainfall (Gxokwe, 2017).

According to (Clark and Fritz, 1997), the isotopic composition of groundwater is usually similar to that of the mean weight annual composition of rainfall. Cappa et al. (2003) and Laar, (2018) described the d-excess value of water of a meteoric origin on a globe scale to be close to 10. The d-excess values of groundwater presented in Table 10, were close to 10 in most instances. Although only a small portion of rainwater reaches the aquifer as recharge after traveling through the vadose zone, precipitation largely influences the isotope signature of groundwater (Bhat et al., 2013). A conclusion that could have been better substantiated if more rainfall samples were available for analysis. No rain samples were available during March

2018, as a result of the drought experienced in the Western Cape region.

The results indicate that surface water samples collected from mid and lower sections of the catchment (evaporated and less depleted samples) had a distinctively different isotopic signature to that of groundwater (p values for $\delta^{18}O$ and $\delta^{2}H$ were less than 0.05), an indication of little to no connection between groundwater and surface water in the lower sections of the catchment. Figures 30 and 31 show a separation between most river and groundwater samples. This lack of connectivity can be attributed to the presence of low yielding geological formations in the lower sections of the catchment. River samples (NJ7, PT1, EST and JS1), collected upstream of the catchment, including those from tributaries of the Nuwejaars River (Jan Swartskraal, and Pietersielieskloof) yielded depleted isotope compositions during both the dry and wet season, similar to those measured for groundwater (p values for $\delta^{18}O$ and $\delta^{2}H$ δ during both seasons were greater than 0.05). As a result these surface water samples clustered with groundwater samples, mostly from boreholes located in the uplands, during both seasons, indicating a connection between groundwater and surface water upstream of the catchment that provides constant base flow to these tributaries.

Groundwater investigations that were conducted concurrently with the current study, focused at understanding the dynamics of groundwater flow within the study area on behalf of the NPR project, also report on the presence of springs within the Table Mountain Group region of the catchment, that provide a constant supply of base flow from deep groundwater systems to tributaries of the Nuwejaars River (Mazvimavi, 2017). The results obtained by the current study provide evidence in the form of isotope data that confirms the role of groundwater in streams in the uplands of the Nuwejaars Catchment. The chemistry of surface water upstream is therefore influenced by groundwater contributions from fresh deep aquifer systems in the Table Mountain Group region of the catchment.

A number of previous studies successfully applied the same methods to establish interactions between groundwater and surface water in different settings (Nonterah, 2015; Gxokwe, 2017; Laar, 2018). In a recent study on the Cape Flats Aquifer, Gxokwe (2017) established interactions between groundwater and surface water during the winter season, however isotope signatures between most groundwater and surface water samples during the dry season differed and did not cluster, indicating no mixing during the dry season. Results from this study, unlike those obtained by the current study, do not indicate a constant interaction between the two water sources during the dry and wet season. Nonterah et al. (2015) established no differences between the isotope signatures of surface water and shallow groundwater in the Sakumo Basin in Ghana, indicating an interaction. Nonterah et al. (2015) also noted that such similarities could also be attributed to similarities in hydrostratigraphy and climatic conditions. The current study did not observed such similarities between shallow groundwater and most surface water samples. The results reported on in previous studies and those obtained by the current study give an indication that stable isotopes of H^2 and O^{18} are useful in the assessment of interactions between groundwater and surface water in different settings.

5.5 Chapter Summary

This chapter reported on findings regarding the physico-chemical and environmental isotope compositions of groundwater and surface water in the Nuwejaars Catchment, collected between July 2017 and July 2018. In order to identify and assess changes in water quality spatially and temporally, graphical representations, such as spatial distribution maps and box plots were generated, while descriptive statistics was used to describe the nature of the data. Independent t Tests and Repeated Measures ANOVA were conducted to evaluate significant differences between groups of water quality data. For further characterization, multivariate statistical methods such as Cluster Analysis and Principle Component Analysis were conducted to identify groups of samples with similar chemical compositions. Characterization methods or tools, such as piper diagrams, stoichiometric analysis and bivariate correlation plots were applied for the analysis and interpretation of hydrochemical data, which allowed for the identification of water type and geochemical process influencing groundwater chemistry in the Nuwejaars Catchment. The results generated from the piper diagrams indicated that groundwater and surface water within the study area is confined to the sodium-chloride water type, suggesting the possibility of an interaction between the two water sources. Bivariate correlation and stoichiometric analysis identified evaporation, ion exchange, reverse ion exchange and the weathering of carbonates and silicates as processes influencing the chemistry of groundwater. To achieve the third and final objective, isotope compositions of groundwater and surface water were assessed to establish interactions between the two sources within the catchment. Isotope results indicated that an interaction between groundwater and surface water exists in the upper regions of the catchment, while no such interactions could be established in the lower regions of the catchment. The following chapter provides a brief summary of the main findings for each objective outlined by the current study.

Chapter 6: Conclusion and recommendations

6.1 Introduction

This study focused on characterizing the water quality of groundwater and surface water in the Nuwejaars Catchment by, firstly assessing the temporal and spatial variations of physico-chemical parameters. This was achieved by conducting several field sampling campaigns that required the measuring of in-situ parameters and the collection of water samples from different sources across the catchment (rivers, boreholes, piezometers, springs and artesian boreholes) for laboratory analysis. The second part of the study focused on the characterization of hydrogeochemical processes influencing groundwater chemistry, which required the analysis and interpretation of hydrochemical data using various characterization tools or methods. Lastly, signatures of stable isotopes of the water molecule δ^2H and $\delta^{18}O$, were assessed to establish interactions between groundwater and surface water.

6.2 Characterization of Physico-chemical parameters

Waters of the Nuwejaars Catchment were generally saline, with high EC values recorded downstream in both surface water and groundwater. Shallow groundwater was generally very saline and recorded the highest concentrations for the majority of the measured parameters during the study period. In the uplands, lower EC concentrations were recorded in deep groundwater and tributaries of the Nuwejaars River. Waters in the uplands, were also slightly acidic, which was attributed to the presence of fynbos and the quartzitic nature of the Table Mountain Group sandstones that underlie the area. Waters in the lower topographical regions of the catchment, were alkaline due to the presence of carbonate bearing formations.

Nutrient concentrations were low and usually within specified limits, however occasional increases in concentrations were observed in both groundwater and surface water. These low nutrient concentrations do not indicate the influence of land-use on water quality. No significant changes in nutrient concentrations over time and between the uplands and the lower regions of the catchment were observed. Major ion concentrations were present in the following order of abundance, $Cl^- > Na^+ > Mg^{2+} > SO^{2-}_4 > Ca^{2+} > HCO^-_3 > K^+$. The lowest and highest concentrations for the majority of the measured parameters were recorded during October 2017 and July 2018 respectively. Spatially concentrations of measured parameters usually increased from the uplands to the lower sections of the catchment. The salinity of waters within the Nuwejaars Catchment, particularly in the lower regions was attributed to reduced river flows, evaporation from irrigated lands, geology type and the lack of groundwater flow due to small hydraulic gradients that favour a longer residence time and ultimately mineralization in groundwater.

Due to high salinities, waters of the Nuwejaars Catchment, particularly downstream did not meet the TWQR specified for domestic use for the majority of the parameters measured during the study period. All waters in the Nuwejaars catchment computed a SAR value that exceeded 2 and can therefore only be used for the irrigation of sodium tolerant crops. Groundwater and surface water are suitable for livestock production.

6.3 Hydrogeochemical characterization

Water type within the catchment was characterized as belonging to the Na-Cl water type, during all four sampling campaigns. The results generated from the piper diagrams confirm the dominance of sodium and chloride ions in waters of the Nuwejaars Catchment. Groundwater of a Na/Cl type is typical for a costal aquifer characterised by saline, deep ancient groundwater. No differences in major ion dominance between groundwater and surface water could be established during the duration of the study. Similarities in water type between the two sources gives an indication of waters originating from the same or similar sources. Bivariate correlation and stoichiometric analysis identified evaporation, ion exchange, reverse ion exchange and the weathering of carbonates and silicates as processes influencing the chemistry of groundwater in the Nuwejaars Catchment.

6.4 Groundwater and surface water interactions

Strong seasonal variations in surface water isotope compositions were observed. Surface water isotope compositions were enriched and evaporated during the dry season, forming a linear pattern below the GMWL. In winter, isotope compositions of surface water were more depleted as a result of lower temperatures. Seasonal variations in groundwater isotope compositions were minimal during the wet and dry season of 2018. Isotope compositions of groundwater upstream yielded similar compositions to those measured for rain, an indication that direct infiltration of rain water is the primary source of groundwater. The majority of surface water did not consist of isotope signatures similar to that of groundwater, indicating no interactions between groundwater and surface water in the majority of the catchment. Isotope signatures of groundwater and that of surface water upstream were similar and therefore clustered together during both seasons. The results therefore confirm that springs upstream provide constant base flow from deep groundwater systems to tributaries of the Nuwejaars River. These connections were also confirmed by the similarities in chemical compositions observed in groundwater and surface water upstream and by the clustering of these samples within the same group in the results generated from the cluster analysis.

6.5 Recommendations

- The maintenance of continuous water quality monitoring of both groundwater and surface water, to generate long term water quality records that will assist decision makers and water resource managers to resolve conflicting issues with regards to water resources that exist within the catchment.
- The installation of rainfall collectors across the catchment, to generate records on isotope compositions of precipitation.
- Further investigations on the chemistry of samples that did not meet the cation-anion balance repeatedly.
- Collaboration between researchers and water resource managers with locals with the objective of protecting water resources that are within an area of ecological value.
- Further investigations that quantify the interactions of groundwater and surface water.
- A detailed investigation on the influence of faults and groundwater flow on water chemistry.

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APPENDICE

Appendix 1a: Physico-chemical parameters of groundwater and surface water, 2017 (Units: Temperature in °C, EC in mS/m, DO in mg/L and pH has no unit).

	July 2017 (Wet Season) n=33				October 2017 (Dry Season) n=32			
Site ID	EC	Temp	pH	DO	EC	Temp	pH	DO
NJ 1	1069.0	16.0	7.9	7.8	998.0	24.5	7.9	8.4
NJ 2	1056.0	19.7	8.4	12.8	106.9	21.0	7.8	9.5
NJ 3	3740.0	17.3	8.1	9.9	103.8	20.2	7.6	8.3
NJ 4	379.0	14.3	7.7	7.5	83.3	21.3	7.1	8.0
NJ 5	214.1	12.8	7.0	8.8	68.3	16.4	6.7	8.1
NJ 6	144.7	18.1	6.9	4.7	78.7	19.0	6.4	5.7
NJ 7	61.9	12.2	6.5	4.9	59.8	17.7	6.2	3.8
NJ 8	1239.0	16.0	7.3	6.2	87.6	18.3	7.7	6.9
VOB	452.0	14.9	7.8	10.6	135.2	19.8	6.8	9.5
PT 1	54.8	17.9	6.4		56.1	22.0	7.9	9.0
JS1					50.1	13.6	6.6	6.9
ETS								
F1	62.4	19.7	5.3	2.9	51.6	21.1	4.9	3.7
F2	55.3	18.8	5.7	1.6	46.0	20.0	5.2	1.9
F3	35.7	18.2	6.1	9.9	24.1	20.6	6.5	9.3
F5	32.0	17.6	6.5		27.4	20.1	7.1	2.5
BH1	1126.0	18.6	7.3	5.6	1023.0	20.0	7.2	7.0
BH2								
BH3	2320.0	18.2	5.5	3.2				
BH 4	1236.0	15.6	7.7	6.4	1224.0	17.7	7.2	4.4
BH 5	1398.0	15.7	8.0	5.8	1329.0	17.8	7.4	4.0
BH 6	377.0	15.2	8.0	6.7	319.0	17.3	7.2	3.7
BH 7	1017.0	14.3	7.8	5.0	653.0	17.2	6.7	4.7
BH 8	281.0	16.2	8.2	2.8	302.0	17.7	7.4	1.9
BH 9	35.0	18.6	5.9	5.7	30.0	17.5	5.9	3.1
BH 10	60.3	17.8	5.8	7.0	34.8	17.4	6.2	2.8
BH 11	77.4	18.7	6.2	-	0.6	19.9	6.3	2.2
BH 12	105.4	18.7	6.7	-	71.2	20.9	6.1	2.8
BH 13	49.8	18.1	6.0	3.6	38.8	19.9	5.3	2.7
BH 14	51.7	15.8	6.0	2.4	43.6	19.7	5.4	2.6
PZ 2	5420.0	17.5	7.4	3.2	2760.0	17.6	6.8	3.9
PZ 8	5730.0	17.6	7.4	3.1	4820.0	17.5	6.5	4.4
PZ 14	3510.0	17.4	6.8	3.7	5740.0	19.2	7.2	5.7
PZ 16	3510.0	18.9	6.6	2.5	2880.0	19.6	6.6	4.0
PZ 26	5200.0	14.5	7.3	4.5	6460.0	19.5	6.7	2.6
PZ19	5200.00	21.40	7.05					

Appendix 1b: Physico-chemical parameters of groundwater and surface water, 2018 (Units: Temperature in °C, EC in mS/m, DO in mg/L and pH has no unit).

	March 2018 (Dry Season) n=33				**July 2018 (Wet Season) n=34**			
Site ID	EC	Temp	pH	DO	EC	Temp	pH	DO
NJ 1	2200.00	25.70	7.93	6.93	2179.90	16.60	8.08	7.14
NJ 2	2590.00	24.20	8.84	11.93	1796.60	17.50	7.68	7.12
NJ 3	538.00	23.50	8.17	8.74	2744.40	17.20	7.79	6.42
NJ 4	197.50	22.80	8.24	7.51	323.90		7.02	6.29
NJ 5	822.00	24.30	7.42	9.56	376.00	15.70	6.54	7.13
NJ 6	153.80	23.70	7.09	5.71	97.70	14.40	6.87	3.56
NJ 7	94.70	23.40	6.69	4.01	68.90	12.10	8.07	3.31
NJ 8	308.00	22.10	8.04	8.12	182.20	14.50	6.15	6.34
VOB	1311.00	22.90	8.02	4.78	244.20	14.70	7.41	6.10
PT 1	64.60	26.00	6.11	7.58	45.15	19.30	5.74	8.64
JS1	90.90	22.90	6.25	3.63	97.80	12.40	5.56	3.36
ETS	35.50	19.40	7.70	8.53	26.50	11.40	5.65	10.23
F1	58.40	20.20	4.96	2.60	45.90	20.50	4.40	1.67
F2					41.32	19.80	5.24	1.24
F3	33.60	21.20	5.31	10.22	20.84	22.80	5.10	4.25
F5	40.80	23.20	5.99	1.81	25.26	18.20	6.62	1.82
BH1	2990.00	21.50	6.92	3.35	2084.20	19.40	6.77	1.31
BH2	6080.00	21.30	7.55	3.91	4318.80	19.60	7.78	3.20
BH3	2069.00	22.50	7.43	3.74	1571.30	19.30	7.71	3.62
BH 4	1707.00	20.10	7.20	3.72	1331.60	17.20	7.09	1.90
BH 5	2270.00	21.50	7.23	3.82	1631.40	17.10	6.94	1.45
BH 6	455.00	20.30	6.97	3.34	456.40	17.10	7.06	1.80
BH 7	1284.00	19.60	6.96	3.21	1059.50	17.00	7.02	1.01
BH 8	304.00	20.80	8.86	3.19	192.90	16.80	7.54	1.84
BH 9	36.20	20.30	5.62	3.53	26.84	17.50	5.31	2.26
BH 10	39.90	21.20	5.42	2.77	38.68	17.80	4.99	4.33
BH 11	71.20	20.40	5.84	2.90	55.00	18.70	4.86	2.07
BH 12	90.70	20.80	6.05	2.30	69.00	19.90	5.78	2.28
BH 13	44.70	18.80	5.70	3.33	37.64	18.90	4.79	1.60
BH 14	46.60	18.50	5.93	3.25	39.83	19.70	5.10	1.04
PZ 2	3100.00	22.40	7.25	3.10	2379.10	18.60	7.07	1.60
PZ 8	5410.00	21.10	6.93	3.63	3991.90	18.60	6.59	1.99
PZ 14	6620.00	21.40	7.03	4.16	4430.90	16.50	6.82	2.35
PZ 16	3300.00	20.30	6.75	3.64	2519.80	19.30	6.58	1.69
PZ 26	6430.00	21.80	7.11	1.11	4407.60	14.90	7.14	5.03

Appendix 2

Appendix 2a: Nutrient concentrations (mg/L) of surface water and groundwater, July 2017 (n= 33).

Site ID	Nitrate	Total Nitrogen	Phosphate	Total Phosphorus
NJ 1	0.1	0.5	2.3	2.5
NJ 2	0.2	1.2	1.7	2.3
NJ 3	0.7	1.1	2.1	2.7
NJ 4	0.3	0.4	1.8	2.0
NJ 5	0.2	0.2	2.3	2.5
NJ 6	0.1	0.5	1.5	2.0
NJ 7	0.1	0.5	1.6	2.0
NJ 8	0.1	0.3	1.4	1.9
VOB	0.3	0.5	0.3	0.7
PT 1	0.2	2.0	2.3	2.5
F1	0.4	5.1	0.7	1.0
F2	0.2	0.5	0.6	0.9
F3	0.3	0.9	0.8	1.3
F4	0.4	0.8	0.4	0.8
F5	0.3	0.5	0.7	0.7
BH1	0.1	4.0	14.9	15.3
BH 3	0.8	0.9	0.4	0.9
BH 4	0.2	0.5	0.2	0.5
BH 5	0.3	0.2	0.4	0.7
BH 6	0.0	0.4	1.5	2.0
BH 7	0.4	0.5	0.2	0.5
BH 8	0.0	0.3	0.8	1.0
BH 9	0.7	0.3	0.1	0.3
BH 10	0.5	0.5	0.0	0.1
BH 11	0.8	0.0	0.7	0.8
BH 12	0.5	0.3	0.9	0.9
BH 13	0.2	0.4	25.7	25.0
BH 14	0.4	1.0	74.0	15.0
PZ 2	0.1	0.1	2.0	2.3
PZ 8	0.5	0.5	3.4	3.9
PZ 14	1.5	1.4	3.5	4.0
PZ 16	3.0	3.2	1.8	1.9
PZ 19	1.3	2.3	10.7	10.6

Appendix 2b: Nutrient concentrations (mg/L) of surface water and groundwater, October 2017 (n= 32).

Site name	Nitrate	Total Nitrogen	Phosphate	Total Phosphorus
NJ 1	0.3	0.5	3.0	3.2
NJ 2	0.0	0.4	3.4	3.0
NJ 3	0.1	0.5	2.3	2.5
NJ 4	0.0	0.4	2.8	3.4
NJ 5	0.2	0.5	2.9	3.5
NJ 6	0.1	0.5	1.9	2.1
NJ 7	0.2	0.5	2.5	2.9
NJ 8	0.0	0.4	2.4	2.7
VOB	0.0	0.3	3.6	3.8
PT 1	0.3	0.5	1.4	1.9
JS1	0.0	0.4	2.7	2.8
F1	0.3	0.5	0.9	1.3
F2	0.3	0.5	0.5	0.6
F3	0.7	0.8	0.5	0.6
F5	0.2	0.6	1.1	1.2
BH1	0.1	0.5	10.0	11.2
BH 4	0.3	0.5	0.9	1.5
BH 5	0.2	0.4	1.1	1.3
BH 6	0.2	0.3	2.8	2.8
BH 7	0.5	0.6	1.9	2.1
BH 8	0.1	0.5	2.8	2.9
BH 9	0.6	0.7	2.3	2.5
BH 10	0.2	0.5	1.4	1.7
BH 11	1.3	1.5	0.4	0.7
BH 12	1.5	1.6	1.3	1.5
BH 13	0.3	0.5	21.6	21.8
BH 14	0.2	0.5	22.6	22.5
PZ 2	0.2	0.4	6.3	6.9
PZ 8	1.0	1.5	1.7	2.3
PZ 14	0.8	0.9	6.0	8.3
PZ 16	0.6	3.4	0.8	2.1
PZ 26	0.6	1.4	2.2	3.0

Appendix 2c: Nutrient concentrations (mg/L) of surface water and groundwater, March 2018 (n = 34).

Site name	Nitrate	Total nitrogen	Phosphate	Total phosphorus
NJ 1	0.6	0.9	0.2	0.7
NJ 2	0.6	4.4	18.6	20.0
NJ 3	0.3	0.5	1.4	3.0
NJ 4	0.3	0.4	0.2	1.0
NJ 5	0.2	0.5	1.7	2.3
NJ 6	0.3	0.5	0.2	0.5
NJ 7	0.2	0.4	0.8	0.8
NJ 8	0.1	0.5	0.4	0.7
VOB	0.2	1.6	11.6	11.8
PT 1	0.2	0.5	0.7	1.2
JS1	0.3	0.5	1.8	1.9
EST	0.3	0.5	1.1	1.0
F1	0.2	0.5	0.0	0.2
F3	0.3	0.4	0.1	0.1
F5	0.3	0.5	0.1	0.2
BH1	0.8	0.5	1.4	1.6
BH2	1.1	1.5	1.5	1.4
BH3	0.3	0.5	2.0	2.4
BH 4	0.4	3.0	0.4	0.8
BH 5	0.5	0.5	0.4	0.9
BH 6	1.0	1.2	0.8	0.9
BH 7	0.2	0.6	0.1	0.6
BH 8	0.2	0.3	1.4	1.3
BH 9	0.7	0.7	0.1	0.9
BH 10	0.5	0.6	2.7	2.9
BH 11	0.4	0.5	0.5	0.6
BH 12	0.6	0.6	3.3	3.9
BH 13	0.1	0.4	1.2	2.1
BH 14	0.0	0.5	3.0	3.6
PZ 2	0.2	0.5	0.4	0.8
PZ 8	0.7	0.8	0.1	0.8
PZ 14	0.6	0.7	0.1	0.3
PZ 16	1.0	1.3	0.2	0.5
PZ 26	0.9	3.2	1.1	1.9

Appendix 2d: Nutrient concentrations (mg/L) of surface water and groundwater, July 2018 (n=34).

Site name	Nitrate	Total Nitrogen	Phosphate	Total phosphorus
NJ 1	0.7	0.7	1.6	1.7
NJ 2	0.1	0.2	1.2	1.5
NJ 3	0.1	0.5	1.0	1.3
NJ 4	0.1	0.1	1.6	1.8
NJ 5	0.0	0.4	3.7	3.9
NJ 6	0.1	2.9	1.7	1.9
NJ 7	0.2	0.4	1.3	1.3
NJ 8	0.1	1.7	1.6	1.7
VOB	0.2	0.5	2.1	2.8
PT 1	0.1	0.4	1.1	1.9
JS1	4.2	18.9	1.4	1.6
EST	0.2	0.4	2.1	2.0
F1	0.3	0.4	0.3	0.6
F2	0.7	1.8	0.4	0.5
F3	0.4	0.5	0.5	0.9
F5	0.3	0.3	0.3	0.7
BH1	0.4	36.7	2.4	3.0
BH2	0.3	0.5	0.9	2.6
BH3	0.2	0.4	0.7	1.1
BH 4	0.1	0.1	0.5	0.7
BH 5	0.0	0.1	0.3	0.9
BH 6	0.1	3.8	0.6	0.8
BH 7	1.5	0.3	7.7	8.3
BH 8	0.5	0.5	5.2	5.0
BH 9	0.2	1.2	1.2	1.9
BH 10	0.7	0.8	2.3	2.8
BH 11	0.2	4.0	0.6	1.2
BH 12	0.1	0.1	1.9	1.8
BH 13	0.1	1.1	4.0	4.3
BH 14	0.3	0.3	3.2	3.5
PZ 2	0.6	0.6	2.1	2.3
PZ 8	0.3	41.2	1.9	3.1
PZ 14	0.5	0.6	1.8	1.9
PZ 16	0.4	21.0	0.7	0.6
PZ 26	0.1	0.5	1.2	1.5

Appendix 3

Appendix 3a: Major ion concentrations of surface water and ground water, July 2017 (n= 34).

July 2017 (Wet Season) Units: meq/L							
Site ID	Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	Cl^{-}	$SO^{2-}{}_4$	$HCO3^{-}{}_3$
NJ 1	5.64	98.52	0.77	13.17	82.55	7.12	2.36
NJ 2	4.69	83.08	0.67	13.99	79.95	5.43	1.21
NJ 3	5.19	88.74	0.79	14.81	90.96	6.08	3.61
NJ 4	1.85	24.58	0.20	6.75	24.69	2.50	0.89
NJ 5	2.10	52.81	0.18	9.05	37.87	3.87	2.59
NJ 6	0.70	39.71	0.08	2.39	7.37	1.52	0.39
NJ 7	0.30	3.52	0.03	1.15	4.10	0.54	0.26
NJ 8	1.15	15.01	0.13	4.11	14.51	2.02	0.33
VOB	2.40	35.23	0.23	7.74	31.14	3.06	0.85
PT 1	0.20	3.35	0.03	0.99	4.03	0.40	0.36
F1	0.25	3.57	0.03	0.91	4.40	0.02	0.33
F2	8.68	280.60	2.07	21.39	318.50	0.40	0.30
F3	0.15	2.26	0.05	0.58	2.90	1.60	0.13
F4	0.10	2.04	0.03	0.58	2.34	0.25	0.20
F5	0.15	1.96	0.03	0.41	2.53	0.23	0.20
BH1	3.34	92.21	2.00	12.34	88.60	0.02	2.98
BH3	10.53	155.50	2.20	18.10	168.10	6.62	4.39
BH4	9.48	91.34	0.28	12.34	98.05	13.43	1.61
BH5	3.39	112.00	0.61	13.17	114.80	6.64	2.98
BH6	1.20	38.28	0.18	3.54	24.41	9.91	3.97
BH7	2.35	80.69	0.31	10.70	70.71	0.81	2.85
BH8	0.95	32.41	0.20	3.05	23.27	5.89	3.28
BH9	0.30	1.91	0.03	0.58	2.78	0.73	0.66
BH10	1.15	2.83	0.08	1.32	3.55	0.87	0.49
BH11	0.35	6.53	0.03	1.15	5.27	0.54	0.82
BH12	2.05	7.18	0.08	1.32	5.93	0.79	1.51
BH13	0.25	2.87	0.03	0.82	4.88	0.33	0.46
BH14	0.25	2.61	0.10	0.82	3.44	0.31	0.43
PZ 7	12.87	393.20	1.28	23.04	526.30	19.59	2.49
PZ 8	12.43	48.15	1.43	23.86	462.80	7.25	2.69
PZ 13	19.01	495.10	2.25	24.69	1156.00	33.50	3.77
PZ 14	3.49	114.20	1.02	15.63	113.40	6.25	1.61
PZ 19	3.29	5.13	0.67	2.39	5.45	0.54	4.16

Appendix 3b: Major ion concentrations of surface water and groundwater, October 2017 (n= 32).

October 2017 (Dry Season) Units: meq/L							
Site ID	Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	Cl^{-}	SO^{2-}_{4}	$HCO3^{-}_{3}$
NJ 1	4.89	51.33	0.82	13.99	87.12	8.60	6.42
NJ 2	0.50	5.83	0.05	1.89	7.40	0.58	0.66
NJ 3	0.45	6.13	0.03	1.89	7.75	0.58	0.62
NJ 4	0.40	5.79	0.03	1.81	7.14	0.56	0.56
NJ 5	0.45	4.92	0.10	1.48	6.01	0.50	0.20
NJ 6	0.45	5.31	0.05	1.56	6.09	0.25	0.46
NJ 7	3.84	95.69	0.77	13.17	104.30	7.79	0.20
NJ 8	0.55	6.22	0.08	1.73	7.44	0.85	0.36
VOB	1.05	8.87	0.13	2.72	10.32	0.02	1.80
PT 1	0.40	4.74	0.05	1.48	5.92	0.48	0.30
JS1	1.05	22.53	0.23	5.84	27.79	3.48	0.20
F1	0.25	3.70	0.05	0.99	4.67	0.40	0.20
F2	0.25	3.74	0.13	1.07	3.91	0.44	0.13
F3	0.15	2.13	0.03	0.58	2.56	0.23	0.10
F5	0.15	2.00	0.03	0.41	2.55	0.02	0.33
BH1	1.85	33.41	0.54	6.09	38.92	6.95	3.61
BH 4	6.44	44.80	0.20	9.88	82.81	8.10	2.26
BH 5	3.49	51.98	0.46	11.52	95.21	12.49	2.29
BH 6	1.10	18.18	0.10	3.62	25.67	1.46	2.00
BH 7	1.50	33.71	0.20	6.58	44.18	4.06	2.00
BH 8	0.65	21.79	0.15	2.63	24.84	0.85	3.61
BH 9	0.30	1.78	0.05	0.58	2.40	0.23	0.36
BH 10	0.70	2.22	0.05	0.66	2.58	0.46	0.20
BH 11	0.40	5.00	0.05	1.23	10.97	0.58	0.43
BH 12	0.85	4.57	0.10	0.99	5.18	0.67	1.31
BH 13	0.20	2.57	0.10	0.74	3.45	0.31	0.33
BH 14	0.45	3.13	0.08	0.99	3.53	0.42	0.49
PZ 2	8.68	290.30	1.97	24.69	399.30	9.95	5.08
PZ 8	10.73	51.33	0.95	21.39	401.80	29.73	2.49
PZ 14	16.87	47.15	1.84	24.69	619.70	49.57	2.85
PZ 16	4.34	54.15	1.02	18.10	215.80	20.97	4.16
PZ 26	21.51	45.63	1.15	23.86	775.10	48.66	2.46

Appendix 3c: Major ion concentrations of surface water and groundwater, March 2018 (n= 34).

March 2018 (Dry Season) Units: meq/L							
Site ID	Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	Cl^{-}	SO^{2-}_{4}	$HCO3^{-}_{3}$
NJ 1	7.44	54.24	1.33	17.28	242.70	17.41	7.77
NJ 2	7.59	55.89	1.02	19.75	284.60	8.43	6.13
NJ 3	1.95	19.70	0.20	7.16	27.62	1.77	1.87
NJ 4	0.95	10.05	0.08	2.88	12.16	0.46	1.31
NJ 5	2.79	40.24	0.23	11.52	56.84	3.10	2.92
NJ 6	0.70	9.35	0.08	2.63	11.51	0.25	0.52
NJ 7	0.50	6.18	0.03	1.98	7.26	0.37	0.49
NJ 8	1.65	17.36	0.15	5.10	20.94	1.33	1.80
VOB	5.19	52.41	0.74	15.63	115.80	9.77	6.69
PT 1	0.30	4.65	0.08	1.32	5.28	0.42	0.10
JS1	0.75	5.66	0.08	2.30	6.91	0.08	1.80
EST	0.15	2.48	0.03	0.66	2.85	0.25	0.13
F1	0.25	3.87	0.05	0.99	4.42	0.37	0.30
F3	0.15	2.31	0.03	0.58	2.80	0.25	0.26
F5	0.35	2.26	0.03	0.41	2.62	0.06	0.16
BH1	4.14	105.20	0.67	16.46	132.70	19.53	5.21
BH2	25.45	2.00	2.25	41.14	507.30	52.36	6.26
BH3	5.19	1.31	0.51	9.05	113.00	17.41	7.64
BH 4	7.29	87.43	0.13	12.34	103.40	11.22	2.69
BH 5	5.89	123.30	0.15	13.99	123.50	18.16	2.46
BH 6	1.50	22.84	0.05	2.39	22.09	1.12	2.69
BH 7	4.49	43.80	0.13	10.70	66.01	7.37	2.23
BH8	0.90	14.92	0.08	1.15	15.86	0.40	5.24
BH9	0.30	1.83	0.03	0.49	2.54	0.21	0.95
BH 10	0.65	2.22	0.05	0.58	2.83	0.35	0.98
BH 11	0.25	2.52	0.03	0.49	3.11	0.40	0.36
BH 12	1.60	5.31	0.08	1.07	5.27	0.69	1.70
BH 13	0.20	2.96	0.41	0.82	3.48	0.31	1.21
BH 14	0.35	2.91	0.15	0.91	3.15	0.23	1.02
PZ 2	4.34	135.20	0.41	12.34	175.80	7.62	6.00
PZ 8	11.18	304.90	0.36	32.92	335.40	29.50	2.92
PZ 14	18.36	366.50	0.69	45.26	482.40	49.03	3.05
PZ 16	4.14	139.60	0.59	18.93	152.20	18.34	5.21
PZ 26	27.69	501.70	0.36	45.26	622.90	42.16	3.87

Appendix 3d: Major ion concentrations of surface water and groundwater, July 2018 (n= 37).

July 2018 (Wet Season) Units : meq/L							
Site ID	Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	Cl^{-}	SO$^{2-}{}_{4}$	HCO3$^{-}{}_{3}$
NJ 1	15.72	190.30	1.64	34.56	348.00	21.82	6.62
NJ 2	19.56	130.50	0.79	35.38	293.00	25.38	2.29
NJ 3	17.81	358.90	0.54	43.61	520.00	27.40	2.88
NJ 4	2.45	23.14	0.15	9.05	33.91	3.31	0.72
NJ 5	2.50	28.80	0.38	9.88	38.70	5.52	1.48
NJ 6	0.90	9.70	0.13	2.96	10.89	1.56	0.43
NJ 7	0.35	5.31	0.05	1.40	5.19	0.62	0.98
NJ 8	1.30	16.44	0.13	5.35	20.25	2.06	0.43
VOB	1.95	19.31	0.15	6.75	27.16	2.75	0.52
PT 1	0.25	4.70	0.05	1.15	4.43	0.58	0.16
JS1	1.35	9.35	0.13	3.62	9.43	2.15	0.36
EST	0.15	3.26	0.03	0.74	3.30	0.29	0.13
F1	0.20	4.61	0.05	0.91	4.25	0.35	0.30
F2	0.20	3.92	0.05	0.82	3.73	0.29	0.59
F3	0.05	1.61	0.03	0.33	1.69	0.15	0.20
F5	0.10	2.09	0.05	0.41	2.70	0.02	0.30
BH1	9.98	337.10	1.54	33.74	391.70	19.07	4.43
BH2	34.58	609.00	2.33	41.97	749.10	44.95	5.57
BH3	13.47	244.70	1.38	23.86	260.40	15.74	7.21
BH 4	12.67	212.10	0.20	22.22	194.00	10.64	2.59
BH 5	12.82	266.40	0.28	28.80	222.90	17.34	2.26
BH 6	2.89	348.00	0.10	6.17	46.81	2.42	2.39
BH 7	9.03	157.70	0.23	23.04	136.80	9.22	2.07
BH8	3.24	17.05	0.10	2.72	20.82	0.19	5.64
BH9	0.45	1.83	0.05	0.58	2.30	0.23	0.98
BH 10	0.50	3.70	0.10	0.99	3.40	0.60	0.46
BH 11	0.25	5.31	0.03	1.07	5.62	0.60	0.36
BH 12	1.10	6.57	0.08	1.23	3.14	0.67	1.02
BH 13	0.20	3.39	0.05	0.82	3.16	0.27	0.26
BH 14	0.25	3.35	0.05	0.91	3.30	0.21	0.39
PZ 2	13.32	353.40	1.23	35.38	433.00	10.06	4.65
PZ 8	22.75	598.10	0.49	43.61	588.40	28.63	1.97
PZ 14	32.88	706.80	0.61	46.90	929.70	45.83	3.08
PZ 16	11.93	375.20	1.07	37.03	485.10	20.30	4.75
PZ 26	37.52	690.50	0.13	47.73	715.50	42.91	2.43
SBH	20.71	647.00	5.42	43.61	600.80	44.85	1.97
RFM	0.15	1.91	0.13	0.41	1.94	0.15	0.62

RFM= rainfall sample SBH = Sea sample

Appendix 4

Sodium adsorption ratio (SAR) values for surface water and groundwater during the study period (n= 29 for July 2017, n= 32 for October 2017, n= 34 for March 2018 and n= 37 for July 2018).

Site ID	July (2017)	October (2017)	March (2018)	July (2018)
NJ 1	38.23	24.49	18.91	32.85
NJ 2	38.93	23.84	19.68	22.19
NJ 3	37.90	27.79	22.04	51.20
NJ 4	28.32	29.44	21.92	21.20
NJ 5	52.65	22.26	31.68	25.55
NJ 6	114.28	24.03	27.43	22.34
NJ 7	23.82	53.11	25.25	30.74
NJ 8	27.18	23.09	22.36	26.69
VOB	31.34	17.61	24.10	21.53
PT 1	33.80	24.12	31.42	37.96
JS1		44.46	15.68	14.79
EST			33.28	43.77
F1	28.83	29.89	31.29	46.43
F2	69.99	30.27		39.43
F3	30.36	28.61	30.94	64.57
F5	26.25	26.84	13.06	41.95
BH1	58.27	37.72	54.91	75.99
BH2			10.44	45.71
BH3	34.06		2.77	42.30
BH 4	22.36	16.39	27.08	39.04
BH 5	69.33	32.65	45.38	48.76
BH 6	64.79	34.02	31.11	242.04
BH 7	71.46	46.68	22.19	40.68
BH8	69.12	67.83	33.51	11.19
BH9	12.93	12.05	12.33	8.28
BH 10	5.25	6.51	6.98	15.06
BH 11	37.66	25.37	20.36	42.83
BH 12	7.34	11.01	6.91	12.27
BH 13	23.23	25.90	29.84	34.20
BH 14	21.14	14.20	16.92	27.08
PZ 2		73.05	65.36	61.91
PZ 8	13.71	14.92	62.77	63.46
PZ 14	69.31	11.76	51.24	54.72
PZ 16		29.47	72.14	72.16
PZ 26		10.21	47.54	48.74
SBH				73.35
RFM				25.67

RFM = rainfall sample SBH = sea sample

Appendix 5

Stable isotope compositions of groundwater and surface water during March and July 2018 (n= 35 for March 2018 and n= 38 for July 2018).

	March 2018 (Dry season)			**July 2018 (Wet Season)**		
Sample ID	δ^2H, in ‰	δ^{18}O, in ‰	d -excess	δ^2H, in ‰	δ^{18}O, in ‰	d -excess
BH1	-23	-4.4	12.2	-23.4	-4.22	10.36
BH2	-8.3	-2.63	12.74	-13.2	-2.57	
BH3	-10.6	-2.85	12.2	-9.4	-2.69	12.12
BH4	-13	-2.82	9.56	-14.5	-3.04	9.82
BH5	-10.3	-2.39	8.82	-15.4	-3.04	8.92
BH6	-6.5	-1.7	7.1	-10.6	-2.2	7
BH7	-5.9	-2.49	14.02	-9.2	-2.74	12.72
BH8	-9	-2.49	10.92	-8.9	-2.7	12.7
BH9	-18.9	-5.22	22.86	-21	-4.76	17.08
BH10	-21.7	-4.8	16.7	-14.9	-3.15	10.3
BH11	-20.6	-5.05	19.8	-20.1	-3.85	10.7
BH12	-21	-4.63	16.04	-20.4	-4.02	11.76
BH13	-20.7	-4.59	16.02	-20.2	-4.01	11.88
BH14	-20.4	-4.51	15.68	-20.1	-4.05	12.3
F5	-18.1	-4.28	16.14	-18.8	-4.68	18.64
F1	-24	-4.61	12.88	-23.3	-4.65	13.9
F2				-18.9	-4.38	16.14
F3	-23.7	-4.63	13.34	-21.4	-4.71	16.28
PZ2	-17.6	-3.26	8.48	-19.7	-3.98	12.14
PZ6	-15.7	-3.51	12.38	-17	-3.61	11.88
PZ8	-17.4	-3.27	8.76	-20	-3.67	9.36
PZ14	-16.9	-3.47	10.86	-15.7	-2.33	2.94
PZ16	-23.6	-5.48	20.24	-24.5	-3.97	7.26
PZ26	-11.8	-2.52	8.36	-12.8	-2.25	5.2
NJ1	20.4	3.41	-6.88	9	0.92	1.64
NJ2	38.8	6.55	-13.6	2.8	-0.5	6.8
NJ3	31.7	5.29	-10.62	4.8	0.61	-0.08
NJ4	22.2	4.27	-11.96	3.7	0.03	3.46
NJ5	7.5	1.13	-1.54	-16.2	-3.23	9.64
NJ6	16.1	2.62	-4.86	-8.4	-2.69	13.12
NJ7	-3.6	-2.42	15.76	-18	-4.17	15.36
NJ8	30.1	5.08	-10.54	-3.8	-1.57	8.76
VOB	38	7.08	-18.64	0.6	-0.98	8.44
JS1	-4.6	-2.02	11.56	-18	-4.21	15.68
ETS	-22.9	-5.12	18.06	-21.1	-4.92	18.26
PT1	-19.3	-4.3	15.1	-16.9	-4.45	18.7
RFM				-25.8	-5.49	18.12
SBH				3.7	0.56	-0.78

RFM = rainfall sample SBH = sea sample

Appendix 6

Appendix 6a: Stoichiometric analysis results for groundwater, July 2017 (n=16).

		July 2017 (Wet Season)		
Site	Na/Cl	Mg/Ca	Ca/ (Ca + S04)	Na/ (Na + Cl)
F1	0.8	3.6	0.9	0.4
F5	0.8	2.7	0.4	0.4
BH1	1.0	3.7	1.0	0.5
BH3	0.9	1.7	0.6	0.5
BH 4	0.9	1.3	0.4	0.5
BH 5	1.0	3.9	0.3	0.5
BH 6	1.6	3.0	0.1	0.6
BH 7	1.1	4.6	0.7	0.5
BH 8	1.4	3.2	0.1	0.6
BH 10	0.8	1.1	0.6	0.4
BH 11	1.2	3.3	0.4	0.6
BH 12	1.2	0.6	0.7	0.5
BH 14	0.8	3.3	0.4	0.4
PZ 7	0.7	1.8	0.4	0.4
PZ 14	1.0	4.5	0.4	0.5
PZ 19	0.9	0.7	0.9	0.5

Appendix 6b: Stoichiometric analysis results for groundwater, October 2017 (n=13).

		October 2017 (Dry Season)		
Site	Na/Cl	Mg/Ca	Ca/ (Ca +S04)	Na/ (Na+Cl)
F1	0.8	4.0	0.4	0.4
F3	0.8	3.8	0.4	0.5
F5	0.8	2.7	0.9	0.4
BH1	0.9	3.3	0.2	0.5
BH 6	0.7	3.3	0.4	0.4
BH 7	0.8	4.4	0.3	0.4
BH 8	0.9	4.1	0.4	0.5
BH 9	0.7	1.9	0.6	0.4
BH 10	0.9	0.9	0.6	0.5
BH 12	0.9	1.2	0.6	0.5
BH 13	0.7	3.7	0.4	0.4
BH 14	0.9	2.2	0.5	0.5
PZ 19	0.9	0.7	0.9	0.5

Appendix 6c: Stoichiometric analysis results for groundwater, March 2018 (n=19).

		March 2018 (Dry Season)		
Site	Na/Cl	Mg/Ca	Ca/ (Ca + S04)	Na/ (Na + Cl)
F1	0.9	4.0	0.4	0.5
F3	0.8	3.8	0.4	0.5
F5	0.9	1.2	0.8	0.5
BH1	0.8	4.0	0.2	0.4
BH 4	0.8	1.7	0.4	0.5
BH 5	1.0	2.4	0.2	0.5
BH 6	1.0	1.6	0.6	0.5
BH 7	0.7	2.4	0.4	0.4
BH 8	0.9	1.3	0.7	0.5
BH 10	0.8	0.9	0.6	0.4
BH 11	0.8	2.0	0.4	0.4
BH 12	1.0	0.7	0.7	0.5
BH 13	0.9	4.1	0.4	0.5
BH 14	0.9	2.6	0.6	0.5
PZ2	0.8	2.8	0.4	0.4
PZ 8	0.9	2.9	0.3	0.5
PZ 14	0.8	2.5	0.3	0.4
PZ 16	0.9	4.6	0.2	0.5
PZ 26	0.8	1.6	0.4	0.4

Appendix 6d: Stoichiometric analysis results for groundwater, July 2018 (n=18).

		July 2018 (Wet Season)		
Site	Na/Cl	Mg/Ca	Ca/ (Ca +S04)	Na/ (Na + Cl)
F1	1.1	4.5	0.4	0.5
F3	1.0	6.6	0.3	0.5
F5	0.8	4.1	0.8	0.4
BH1	0.9	2.4	0.4	0.5
BH 4	1.1	1.8	0.5	0.5
BH 5	1.2	2.2	0.4	0.5
BH 7	1.2	2.6	0.5	0.5
BH 8	0.8	0.8	0.9	0.5
BH 9	0.8	1.3	0.7	0.4
BH 10	1.1	2.0	0.5	0.5
BH 11	0.9	4.3	0.3	0.5
BH 13	1.1	4.1	0.4	0.5
BH 14	1.0	3.6	0.5	0.5
PZ2	0.9	2.7	0.6	0.4
PZ 8	0.8	1.9	0.4	0.5
PZ 14	0.8	1.4	0.4	0.4
PZ 16	1.0	3.1	0.4	0.4
PZ26	0.8	1.3	0.5	0.5

Appendix 7

Appendix 7a: Independent t Test results for physico-chemical variables, comparisons between concentrations in the upper and lower regions of the catchment. (n = 10 for July 2017, n=11 for October 2017 and n= 12 for March and July 2018).

Surface water

		Equality of variances		t Test of equality of means		
Parameter	**Sampling month**	**F**	**Sig.**	**T**	**df**	**p value**
pH	July (2017)	0.14	0.72	2.49	8	0.038
	October (2017)	1.95	0.20	0.22	9	0.832
	March (2018)	2.65	0.13	2.43	10	0.036
	July (2018)	1.08	0.32	2.39	10	0.038
EC	July (2017)	1.45	0.26	1.42	8	0.192
	October (2017)	1.44	0.26	1.56	9	0.152
	March (2018)	1.44	0.26	3.56	10	0.005
	July (2018)	4.47	0.06	3.41	10	0.007
Temp	July (2017)	0.06	0.81	0.45	8	0.662
	October (2017)	0.24	0.64	1.36	9	0.206
	March (2018)	1.87	0.20	1.12	10	0.287
	July (2018)	3.66	0.08	1.65	10	0.130
DO	July (2017)	1.25	0.30	1.70	7	0.133
	October (2017)	0.83	0.39	1.52	9	0.163
	March (2018)	0.06	0.81	1.07	10	0.309
	July (2018)	5.76	0.04	-0.08	5	0.936
Sodium	July (2017)	5.44	0.05	1.75	2	0.203
	October (2017)	2.02	0.19	-1.01	9	0.338
	March (2018)	1.15	0.31	3.46	10	0.006
	July (2018)	7.60	0.02	3.54	9	0.006
Calcium	July (2017)	1.14	0.32	2.43	8	0.041
	October (2017)	0.04	0.85	-0.52	9	0.613
	March (2018)	0.16	0.70	3.11	10	0.011
	July (2018)	1.72	0.22	3.41	10	0.007
Magnesium	July (2017)	2.42	0.16	2.10	8	0.069
	October (2017)	1.15	0.31	-0.75	9	0.472
	March (2018)	0.46	0.51	3.27	10	0.008
	July (2018)	0.64	0.44	3.61	10	0.005
Potassium	July (2017)	0.08	0.79	2.63	8	0.030
	October (2017)	0.03	0.88	-0.96	9	0.362
	March (2018)	2.87	0.12	2.24	9	0.052
	July (2018)	1.26	0.29	3.39	10	0.007
Chloride	July (2017)	0.42	0.54	1.88	8	0.097
	October (2017)	1.18	0.31	-0.87	9	0.408
	March (2018)	3.48	0.09	3.17	10	0.010
	July (2018)	8.98	0.01	3.75	9	0.005

Sulphate	July (2017)	4.46	0.07	2.33	8	0.048
	October (2017)	0.00	0.99	-1.36	9	0.207
	March (2018)	1.91	0.20	2.53	10	0.030
	July (2018)	2.05	0.18	3.41	10	0.007
Bicarbonate	July (2017)	0.71	0.42	0.70	8	0.506
	October (2017)	2.54	0.14	2.46	10	0.034
	March (2018)	1.05	0.33	2.61	10	0.026
	July (2018)	1.11	0.32	2.18	9	0.057
Nitrate	July (2017)	1.2	0.3	1.1	8	0.300
	October (2017)	1.1	0.3	-0.3	9	0.762
	March (2018)	3.3	0.1	1.6	10	0.133
	July (2018)	7.8	0.0	-0.9	4	0.395
Total nitrogen	July (2017)	6.8	0.0	-0.5	2	0.632
	October (2017)	0.7	0.4	-0.2	9	0.878
	March (2018)	4.8	0.1	1.2	10	0.264
	July (2018)	7.9	0.0	-1.0	4	0.380
Phosphate	July (2017)	0.2	0.7	-0.1	8	0.909
	October (2017)	0.0	1.0	1.6	9	0.142
	March (2018)	10.7	0.0	1.4	6	0.211
	July (2018)	1.3	0.3	0.8	10	0.442
Total phosphorus	July (2017)	0.6	0.5	-0.1	8	0.938
	October (2017)	0.4	0.5	1.4	9	0.185
	March (2018)	9.6	0.0	1.6	6	0.163
	July (2018)	4.2	0.1	1.0	10	0.339

Appendix 7b: Independent t Test results for physico-chemical variables, comparisons between concentrations in the upper and lower regions of the catchment. (n = 17 for July 2017, n=16 for October 2017, n= 17 for March 2018 and n= 18 for July 2018).

Deep groundwater						
		Equality of variances		t Test for equality of means		
Parameter	**Sampling month**	**F**	**Sig.**	**T**	**df**	**p value**
pH	July (2017)	1.63	0.22	-4.33	15	0.001
	October (2017)	8.23	0.01	-5.15	12	< 0.001
	March (2018)	0.02	0.89	-7.55	15	< 0.001
	July (2018)	1.31	0.27	-7.74	16	< 0.001
EC	July (2017)	3.88	0.07	-10.37	15	< 0.001
	October (2017)	0.21	0.66	-5.57	14	< 0.001
	March (2018)	5.45	0.03	-9.43	8	< 0.001
	July (2018)	4.21	0.06	-10.44	16	< 0.001
Temp	July (2017)	2.16	0.16	3.10	15	0.007
	October (2017)	0.28	0.61	2.85	14	0.013
	March (2018)	0.40	0.54	-0.80	15	0.439
	July (2018)	0.02	0.90	2.19	16	0.044
DO	July (2017)	3.43	0.09	-0.71	12	0.489
	October (2017)	0.00	0.99	-1.25	14	0.232
	March (2018)	2.87	0.11	-0.58	15	0.571
	July (2018)	0.07	0.80	0.44	16	0.666
Sodium	July (2017)	1.31	0.27	-4.59	15	< 0.001
	October (2017)	0.00	1.00	-12.24	14	< 0.001
	March (2018)	12.27	0.00	-3.24	7	0.013
	July (2018)	1.44	0.25	-10.95	16	< 0.001
Calcium	July (2017)	1.05	0.32	-3.22	15	0.006
	October (2017)	0.48	0.50	-5.06	14	< 0.001
	March (2018)	0.48	0.50	-6.09	15	< 0.001
	July (2018)	0.48	0.50	-6.09	15	< 0.001
Magnesium	July (2017)	0.06	0.81	-4.34	15	0.001
	October (2017)	1.45	0.25	-8.91	14	< 0.001
	March (2018)	4.69	0.05	-6.14	8	< 0.001
	July (2018)	4.14	0.06	-9.45	16	< 0.001
Potassium	July (2017)	0.01	0.93	-3.46	15	0.004
	October (2017)	0.16	0.69	-4.57	14	< 0.001
	March (2018)	1.12	0.31	-2.58	15	0.021
	July (2018)	18.50	0.00	-4.96	16	< 0.001
Chloride	July (2017)	0.19	0.67	-4.10	15	0.001
	October (2017)	0.53	0.48	-9.58	14	< 0.001
	March (2018)	7.10	0.02	-8.20	8	< 0.001
	July (2018)	7.42	0.02	-9.34	8	< 0.001
	July (2017)	2.81	0.11	-2.18	15	0.045

Sulphate	October (2017)	0.38	0.55	-4.97	14	< 0.001
	March (2018)	4.77	0.05	-5.41	9	< 0.001
	July (2018)	1.57	0.23	-5.28	16	< 0.001
Bicarbonate	July (2017)	2.76	0.12	-6.86	15	< 0.001
	October (2017)	2.74	0.12	-6.78	14	< 0.001
	March (2018)	7.33	0.02	-5.80	13	< 0.001
	July (2018)	0.01	0.93	-8.63	16	< 0.001
Nitrate	July (2017)	0.58	0.46	1.48	15	0.159
	October (2017)	5.12	0.04	2.01	12	0.068
	March (2018)	3.23	0.09	-1.51	15	0.151
	July (2018)	1.54	0.23	-0.34	16	0.738
TN	July (2017)	0.00	0.96	-0.03	15	0.976
	October (2017)	4.84	0.05	2.16	11	0.055
	March (2018)	10.24	0.01	-1.53	7	0.169
	July (2018)	5.46	0.03	-0.94	7	0.378
Phosphate	July (2017)	3.50	0.08	0.85	15	0.411
	October (2017)	3.69	0.08	0.52	14	0.608
	March (2018)	7.15	0.02	0.43	12	0.677
	July (2018)	3.53	0.08	-0.84	16	0.416
TP	July (2017)	1.21	0.29	0.44	15	0.665
	October (2017)	3.17	0.10	0.47	14	0.645
	March (2018)	15.41	0.00	0.68	10	0.513
	July (2018)	2.61	0.13	-1.02	16	0.323

Appendix 7c: Repeated measures ANOVA results, testing for temporal variations in variables of surface water during July 2017- July 2018 (n = 10).

Surface water						
Parameter		**Sum of Squares**	**Df**	**Mean Square**	**F**	**p value**
Temp	Time	439.77	3	146.59	68.13	< 0.001
	Error	58.09	27	2.15		
DO	Time	23.81	3	7.94	5.04	0.008
	Error	37.82	24	1.58		
pH	Time	1.60	2	0.84	1.66	0.220
	Error	8.70	17	0.51		
EC	Time	2.35	3	0.78	7.94	0.001
	Error	2.67	27	0.10		
Sodium	Time	1.46	3	0.49	2.72	0.064
	Error	4.85	27	0.18		
Calcium	Time	1.30	1	0.91	3.16	0.089
	Error	3.70	13	0.29		
Potassium	Time	0.81	1	0.57	1.64	0.231
	Error	4.47	13	0.35		
Magnesium	Time	1.15	2	0.75	3.43	0.072
	Error	3.01	14	0.22		
Chloride	Time	1.58	3	0.53	2.70	0.066
	Error	5.26	27	0.19		
Sulphate	Time	3.23	2	2.08	4.02	0.050
	Error	7.24	14	0.52		
Bicarbonate	Time	0.95	3	0.32	3.03	0.047
	Error	2.82	27	0.10		
Nitrate	Time	0.82	3	0.27	0.34	0.799
	Error	22.04	27	0.82		
Total nitrogen	Time	0.83	3	0.28	0.33	0.802
	Error	22.32	27	0.83		
Phosphate	Time	0.04	3	0.01	0.01	0.998
	Error	29.73	27	1.10		
TP	Time	0.03	3	0.01	0.01	0.999
	Error	30.67	27	1.14		

Appendix 7d: Repeated measures ANOVA results, testing for temporal variations in variables of groundwater during July 2017- July 2018 (n = 15).

Deep groundwater

Parameter		Sum of Squares	Df	Mean Square	F	p value
Temp	Time	2.88	3	0.18	23.60	< 0.001
	Error	0.03	42	0.00		
DO	Time	1.20	3	0.40	24.27	< 0.001
	Error	0.54	33	0.02		
pH	Time	0.02	3	0.01	13.43	< 0.001
	Error	0.03	42	0.00		
EC	Time	0.63	1	0.55	3.08	0.094
	Error	2.88	16	0.18		
Sodium	Time	0.84	1	0.61	6.92	0.010
	Error	1.71	19	0.09		
Calcium	Time	0.21	2	0.13	1.72	0.205
	Error	1.67	21	0.08		
Potassium	Time	0.09	2	0.05	0.59	0.547
	Error	2.08	25	0.08		
Magnesium	Time	0.25	2	0.13	4.39	0.022
	Error	0.80	28	0.03		
Chloride	Time	0.13	1	0.08	1.70	0.210
	Error	1.03	21	0.05		
Sulphate	Time	0.02	1	0.02	0.02	0.898
	Error	11.58	15	0.75		
Bicarbonate	Time	0.29	3	0.10	4.41	0.009
	Error	0.93	42	0.02		
Nitrate	Time	0.15	3	0.05	0.05	0.983
	Error	38.31	42	0.91		
Total nitrogen	Time	0.09	3	0.03	0.03	0.994
	Error	47.51	42	1.13		
Phosphate	Time	450.02	1	413.97	1.77	0.204
	Error	3559.12	15	233.86		
Total phosphorus	Time	0.16	2	0.08	0.09	0.922
	Error	25.58	29	0.88		

Appendix 7e: Independent t Test results for isotope compositions, comparisons between groundwater and surface water upstream (n=13 for March 2018 and n= 15 for July 2018).

		Equality of variances		t Test for equality of mean		
Sampling month	**Parameter**	**F**	**Sig.**	**t**	**Df**	**p value**
March (2018)	$\delta^{2}H$ ‰	6.52	0.03	1.83	4	0.140
	$\delta^{18}O$ ‰	8.17	0.02	1.60	4	0.185
July (2018)	$\delta^{2}H$ ‰	4.94	0.04	-1.40	4	0.227
	$\delta^{18}O$ ‰	3.29	0.09	-0.78	13	0.448

Appendix 7f: Independent t Test results for isotope compositions, comparisons between groundwater and surface water downstream (n =21 for March and July 2018).

		Equality of variances		t Test for equality of mean		
Sampling month	**Parameter**	**F**	**Sig.**	**t**	**Df**	**p value**
March (2018)	$\delta^{2}H$ ‰	7.62	0.01	-8.25	7	< 0.001
	$\delta^{18}O$ ‰	7.14	0.02	-8.77	7	< 0.001
July (2018)	$\delta^{2}H$ ‰	2.50	0.13	-4.93	19	< 0.001
	$\delta^{18}O$ ‰	7.12	0.02	-3.55	7	0.009