HYDROGEOLOGICAL INVESTIGATIONS OF GROUNDWATER AND SURFACE WATER INTERACTIONS IN THE BERG RIVER CATCHMENT, WESTERN CAPE, SOUTH AFRICA

by

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DECLARATION

I, **Seiphi Prudance Mabokela**, declare that the contents of this dissertation represent my own unaided work, and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed

Date

ABSTRACT

It is well established that the quality of fresh water resources has been and still is deteriorating at an escalated rate globally affecting the chemical, physical and biological composition of water. As a result, fresh water has thus become a rare commodity which is crucial for the survival of any living organism on earth. Fresh water is found in groundwater aquifers and surface water resources such as rivers, streams, lakes and dams however, these resources only comprise 0.3% of fresh water that is available for human consumption out of the 71% water that constitute the earth. The remaining quantity of water found in oceans and seas requires expensive processes of desalination in order to become potable for human use. Therefore, the deteriorating quality of fresh water is escalating the already existing problem of water scarcity and as such, in the nearer future the demand will surpass supply of fresh water. Moreover, drinking water from surface water bodies have to be purified first to meet the drinking water standards before consumption. This nonetheless, does not eliminate that groundwater also have to meet drinking water standards.

Groundwater and surface water have been considered as isolated components of the hydrological cycle for centuries in the application of water resources management. This has therefore resulted in the lack of understanding of the two hydrological components. The lack of understanding therefore continues to create gaps in determining important information such as factors impacting on the quantity and quality of groundwater in particular. The complexities in determining the interactions between surface water and groundwater has thus led to surface water receiving much attention in poorer countries as it is readily available and accessible to study as opposed to groundwater.

In South Africa, much of the water used is obtained from surface water bodies like rivers, springs and earth dams. The dynamics of surface and groundwater chemical transfers has not been thoroughly studied and well understood in the country. Such a case is also observable from the Berg River catchment (BRC) wherein surface water quality have been severely studied, while on the other hand groundwater chemistry and quality in

relation to the natural setting remains questionable. This study therefore provides an investigation of the interactions of surface and groundwater in the BRC. The study focused on three objectives as follows: to a) investigate the role that geology and soils play on water chemistry in the BRC, b) to identify BRC surface and groundwater chemical trends and c) to identify the geochemical processes controlling surface and groundwater chemistry in BRC. This study employed a combination of techniques (i.e. hydrochemical, environmental tracer analysis and hydrogeological mapping).

This study was carried out using three types of research designs namely i) Experimental research design; ii) Field research design and meta-analysis research design. Furthermore, the study made use of hydrochemical data ranging from 2003 to 2013 obtained from the National Water Monitoring Database owned and maintained by the Department of Water and Sanitation and data which was sampled in 2016 and analyzed using the ICP-MS Technique. This method was employed when analysing the water samples for the major cations and anions in the laboratory using Perkin Elmer ICP-OES Optima 5300 DV (to analyze cations) as well as ThermoFischer Scientific Gallery plus discreet analyser (to analyze anions). Ground Water Chart, Arc-GIS and Geosoft (Oasis Montaj) were further employed to model the data.

Groundwater Water Chart was used to model hydrochemical facies which displays various water types while Geosoft (Oasis Montaj) was used to grid the nitrates concentrations in both surface and groundwater data to establish the trends and correlations. The color intensity and scale were used to denote the concentration magnitude of analytes understudied. Finally, Arc GIS was used for creation of maps that were used to indicate direction of water flow, sampling points (location), correlation, trends as well as vulnerable areas which are more prone to contamination.

From the analysis and interpretation, the hydrochemical facies indicated that in the upper Berg River Catchment, there is very minimal interaction between surface and groundwater systems. Other water types that were found in the groundwater either than NaCl were barely found in surface water and vice versa as it was observed that, surface water samples have both NaCl and Mixed-CaMgCl while groundwater have three additional water types to those of surface including $CaHCO_3$, Mixed $CaNaHCO_3$ and CaCl. This may be due to the underlying consolidated hard rock formations (granitic rocks) having less geohydrological properties like fractures and voids.

The Middle Berg however, indicated a degree of interaction with sharing of constituents between the two water systems. Most of the water types found in borehole data were also found in the surface water. This can be explained with reference to the structural geology of the area in which a northwest-trending strike-slip faults of the Piketberg-Wellington faults occurred which gave rise to more permeability and movement of water.

Moreover, the Lower Berg indicated only NaCl water type. It is worth note taking that the Lower Berg is situated near the river mouth whereby there is mixing of river and sea water. This notion therefore further explains the NaCl being the sole water type in the area. In surface water this may have further been exacerbated by means of sea spray. With reference to groundwater, there may have been a possibility of sea water intrusion also enhanced by the faulting of rocks originated from the Colenso fault.

DEDICATION

This thesis is dedicated to me and my dearest mother

Ramokone Dinah Mabokela. Thank you for being the wind beneath my wings Mother.

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I wish to send my deepest gratitude to:

- The Almighty God for granting me the will and strength to never give up while undertaking this study and complete it successfully.
- My supervisor, Dr. Ntokozo Malaza, for his knowledge, guidance, and for believing in me and most importantly for always pushing and never giving up on me. May God grant you, Dr. Malaza more strength to carry out your work as impeccably as you have been and may He bless you more.
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- The Department of Water and Sanitation

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LIST OF ABBREVIATIONS

Abbreviation	Description
BRC	Berg River Catchment
CGS	Council for Geoscience
CSG-A	Cape Suit Granite-Aquifer
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conducitivity
GC-IRMS	Gas Chromatography- Isotopic Ratio Mass Spectrometry
GIS	Geographical Information System
GPS	Global Positioning System
KG-A	Klipheuwel Group-Aquifer
MG-A	Malmesbury Group-Aquifer
TMG-A	Table Mountain Group-Aquifer

CHAPTER 1: INTRODUCTION

1.1 Background

It is well established that the quality of fresh water resources has been and still is deteriorating at an escalated rate globally affecting the chemical, physical and biological composition of water. As a result, fresh water has thus become a rare commodity which is crucial for the survival of any living organism on earth (Tombo, 2010). Fresh water is found in groundwater aquifers and surface water resources such as rivers, streams, lakes and dams however, these resources only comprise 0.3% of fresh water that is available for human consumption out of the 71% water that constitute the earth (Tombo, 2010 and Khatri & Tyagi (2015). The remaining quantity of water found in oceans and seas requires expensive processes of desalination in order to become potable for human use. Therefore, the deteriorating quality of fresh water is escalating the already existing problem of water scarcity as Khatri & Tyagi (2015) highlighted that in the nearer future the demand will surpass supply of fresh water.

According to Khatri & Tyagi (2015), although water may not contain organic nutrients and calories, safe water is still a necessity for all living organisms. More often people utilize the term “safe water” although the term is relative. The desired water quality varies with different uses and the criteria used to assess water quality also vary. For instance, Khatri & Tyagi (2015) highlight that the water quality required for crop irrigation varies from the water quality needed for drinking; hence different water quality standards exist. In the modern day however, the drinking water quality have devastatingly decreased which result in many water borne diseases as well as wars for water resources and in worst cases, death result from such.

A recent example can be pointed out to the area of Qwaqwa, a small village in the North-Eastern Free State Province in South Africa, where the community violently damaged municipal properties in trying to raise their demand for safe drinkable water (DWS, 2020). In the same area, a child drowned while trying to access water from a nearby river even though the quality of water from the river is unknown to the residents (News24, 2020). Musingafi (2014) stressed that water from surface water bodies may seem clean and safe to drink but more often it is not; hence drinking water from surface water bodies have to be purified first to meet the drinking water standards before consumption. This nonetheless, does not eliminate that groundwater also have to meet drinking water standards.

The surface and groundwater quality is a function of natural setup and processes as well as anthropogenic activities collectively. According to Khatri & Tyagi (2015) human influences towards the quality of water are a result of the economic activities such as application of fertilizers, irrigation, construction sites, mining operations, sewage and industrial discharge, leaching of contaminants from land fill sites and feedlots of livestock farming amongst many others. On the other hand, groundwater quality is influenced by means leaching of organic matter and nutrients from soil, weathering of bedrock minerals, atmospheric processes involving evapotranspiration, deposition of dust and salts by wind or water. All these processes possess a great potential to introduce contaminants in both surface and groundwater systems (Khatri & Tyagi, 2015). Both water systems can further be influenced by physiographical factors such as topography, land cover, climate, stream geomorphology, as well as the positioning of surface water features relative to subsurface water flow paths in catchments (Madlala, 2015).

As a result, effective water quality management requires a thorough understanding of how and why chemical composition varies across the catchment. Understanding these many forces playing a role on water quality is thus essential for development of effective water quality management strategies as per Section 9 of the National Water Act, 36 of 1998. According to Lintern et al. (2017), immense studies linking anthropogenic activities and water quality have been conducted in the BRC. However, there has been less studies on the natural setting particularly geology and soil types influencing the chemistry of water in the BRC. This research thus aims to lessen this gap by discussing the hydrogeochemical interactions between surface and groundwater with respect to geologic setting and soils in the BRC. This study intends to be of good use to water users, catchment managers and researchers to develop water quality management strategies and models.

1.2 Location of the Berg River Catchment

The Berg River Catchment is found in the Western Cape Province broadening about 270km from Jonkershoek and Franschhoek mountains flowing in a north westerly direction where it discharges into the Atlantic Ocean at Laaiplek (Görgens & Clercq, 2005 and Rossouw & Malan, 2007) (Figure 1.1). From the headwaters, the river flows north and joins with the Franschhoek River in the Franschhoek valley where it is further merged by two more tributaries: the Wemmershoek River to the east and the Banhoek River to the west (Görgens & Clercq, 2005).

Furthermore, the Berg River flows through Paarl and Wellington where it is joined by the Krom River tributary from the eastern direction (Görgens & Clecq, 2005). In the north of Wellington, the Berg River is connected to several other tributaries namely: Klein Berg River, Kompanjies River and the Twenty Four Rivers (Görgens & Clercq, 2005 and Rossouw & Malan, 2007). Further southwards it is joined by the Boontjies River where it begins to flow westwards between the Obiekwa and Voëlvlei mountains into the Berg River Valley and joins the Berg River to the west of Saron (Görgens & Clercq, 2005 and Western Cape Government, 2012). The Berg River then flows over the Misverstand Weir in which upstream of the weir, the river is joined by the tributaries that drain the areas north of Porterville and Moorreesburg (Görgens & Clercq, 2005). The river then flows in a north-westward direction and drains into the Atlantic Ocean at Velddrift (Görgens & Clercq, 2005; Rossouw & Malan, 2007 and Western Cape Government, 2012).

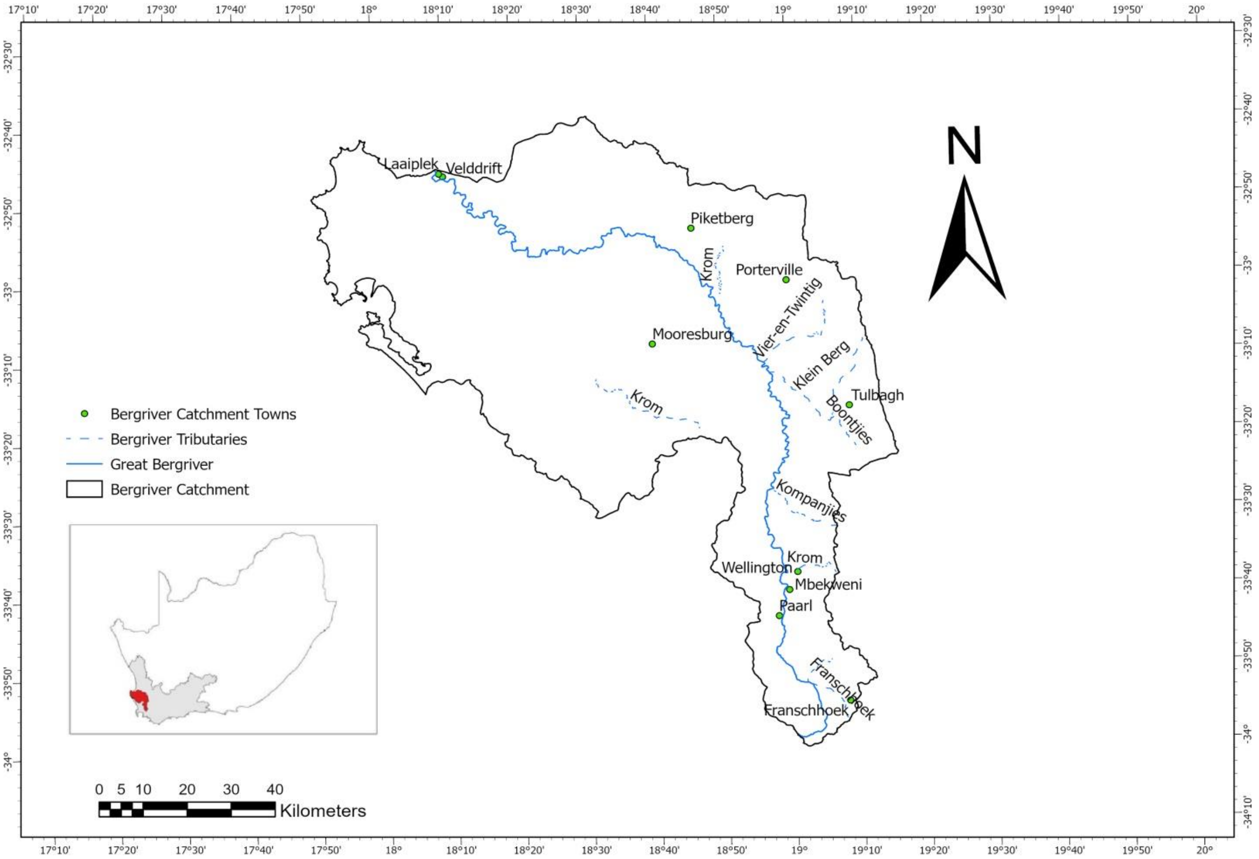

Figure 1.1: Location of the Berg River Catchment

1.3 Climate and vegetation

The climate in the Berg River catchment is a typical Mediterranean climate of the Western Cape Region. Water Institute of Southern Africa-WISA (2012) stated that this zone is classed as a humid zone and receive significant amount of winter precipitation and extreme summer evaporation. In addition, Görgens & Clercq (2005) highlighted that precipitation in the catchment occurs as a result of the cold fronts approaching from the southwest particularly the Antarctic. In the high lying areas of the Groot Drakenstein, the Mean Annual Precipitation (MAP) is usually above 1500mm but decreases steadily to less than 500mm further northwards towards the mouth of the river. The MAP then drops further to below 300mm at the river mouth in Veldrift (Midgley et al., 1994).

Furthermore, the Mean Annual Evaporation (MAE) in the southern and western regions of the catchment ranges from 1400mm to over 1600mm in the northeast (Görgens &

Clercq, 2005). On the other hand, Midgley et al. (1994) noted that there are significant seasonal variations in monthly evaporations which fall typically between 40mm and 50mm in winter and 230mm – 250mm in the summer months. Moreover, the snow that falls on the peaks and upper slopes of the mountains during intermittent cold weather in the winter also contributes to the flow of the river (Midgley et al., 1994). In the connecting valleys, rainfall varies from 900mm to 1200mm annually, but drops to between 400mm and 500mm in the hilly plain through which the river flows most of its length, and to even less when it approaches the sea (Midgley et al., 1994).

The vegetation comprises the typical fynbos and renosterveld plant species which are dominated by shrubs and very short trees distributed in irregular patches as shown in Figure 1.2 (O'Callaghan, 1994). O'Callaghan (1994) added that the patchy and irregular distribution patterns possibly result from an inconsistent relationship between species distribution and salinity, tidal inundation and/or competitive interactions. The shrubs are characterised by their short height, toughness and grey leaves. There is also an abundant grass and flowers during spring season (O'Callaghan, 1994). Towards the estuary, the catchment consist of small saltmarshes which are often more green than the upper Berg River catchment (O'Callaghan, 1994).

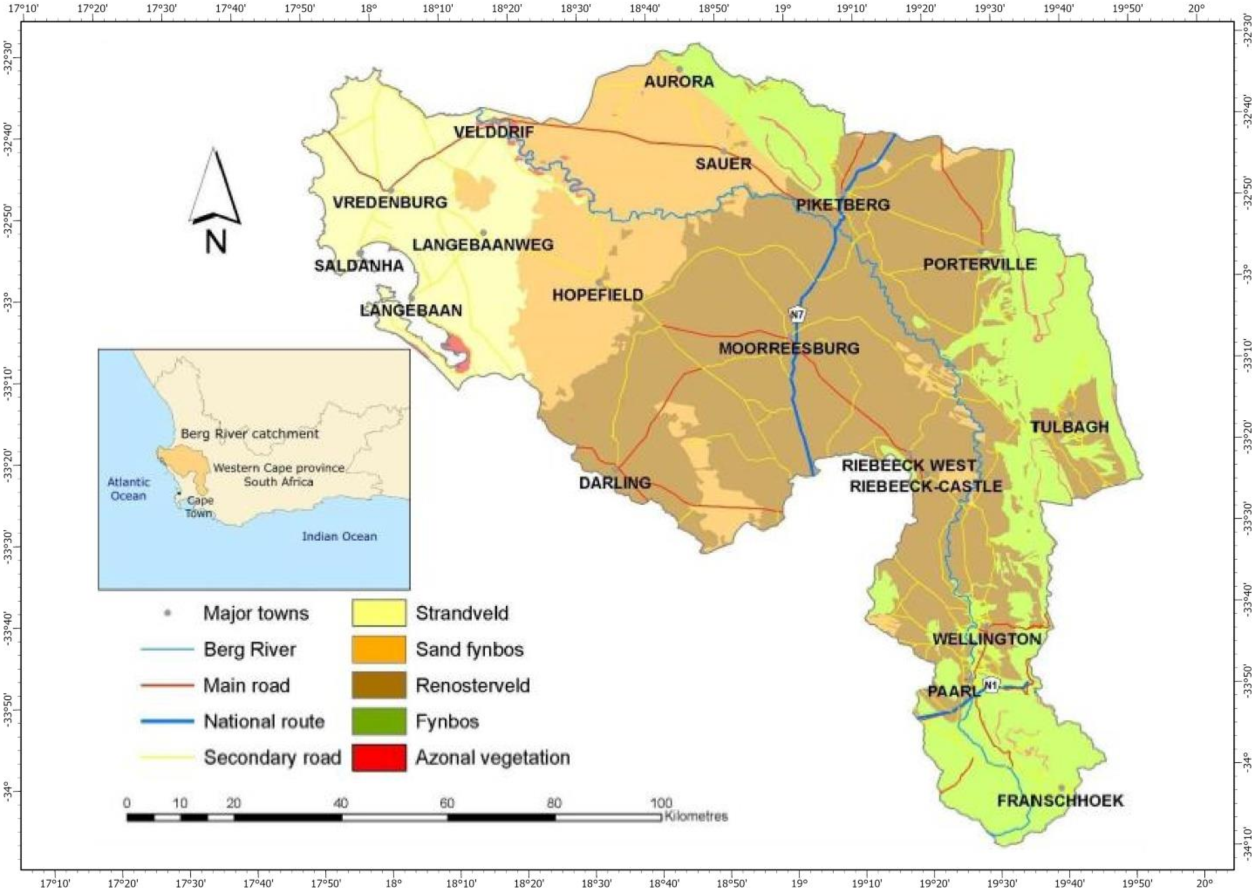

Figure 1.2: BRC vegetation map (Stuckenberg, 2012)

1.4 Land use activities

The land use in the BRC can be divided into four types namely: i) agriculture which comprise about +60% of the catchment, ii) forestry which is about, 1% iii) urban settlements which takes up about +2.5% and iv) natural which takes further +36% of the catchment (Cullis et al., 2019). Furthermore, the agricultural land is further divided into two sectors namely i) dry land farming activities which comprise about 53% as well as ii) irrigated land which takes up +7%. The catchment however, has recently experienced high volume of population increase which results in urbanization in the Paarl, Tulbagh and Wellington areas (Cullis et al., 2019).

Apart from the growth of urban settlements which may supersede other land uses activities in the catchment in the nearer future, the current dominant land use activity in the BRC is agricultural activities particularly the vine yards which occur in the upper, middle and lower segments of the catchment (Cullis et al., 2019). According to Cullis et al. (2019) the diversity of agricultural activities in the BRC can be subdivided into a number of smaller homogeneous production areas (shown in Table 1.2). These include:

1. Franschhoek (Upper Berg): Wine grapes, stone fruit and pome fruit
2. Paarl (Lower-Middle Berg): Table grapes, wine grapes and stone fruit
3. Wellington (Middle Berg): Wine grapes, table grapes and stone fruit
4. Swartland (Middle-Lower Berg): Winter cereals, small stock and potatoes.

Amongst other produces not listed above are oranges and lemons, apricot, almonds, olives, apples, cherries, wheat and tobacco which are farmed at small scale compared to the ones listed above (Nitsche et al., 2006). Table 1.1 below indicates the actual and relative size of the various farming activities and the percentage of produce to that of South Africa. The area has proven to be essential producer of table grapes and wine grapes, as in this area; there are 120 out of a total of only 493 private wine cellars across the whole of South Africa. This shows the agricultural value adding that is produced within the Berg River area, particularly in terms of export earnings and tourism.

Table 1. 1: The actual and relative (to South Africa) contribution of table grape production, wine grape production and fruit production of the Berg River area. Sources: SATI (2017), SAWIS (2016) and Vinpro (2017)

Agricultural Produce	**Actual**	**% of South African total**
Table grapes (4.5kg carton equivalent)	15,426,175	23%
Wine grapes (number of vines)	45,876,435	16.17%
Fruit: Nectarines (ha)	210	9.9%
Pears (ha)	132	1.1%

Table 1. 2: Farm size and land use for the typical farm of each relatively homogenous area (Cullis et al., 2019)

Area	Farm Size	Cultivated Land
Franschhoek	150 ha	69%
Paarl	200 ha	69%
Wellington	130 ha	60%
Swartland	850 ha	822%

Although BRC has shown to be adding an enormous economic value to the Western Cape Province, Cullis et al. (2019) however highlighted that with the deterioration of the water quality in the catchment; in the nearer future agricultural activities might be seen vanishing and or rather producing low quality crops. Figure 1.3 and Figure 1.3 below shows a decline in the overall agricultural land use activities between 2006 and 2015. This might further be exacerbated by an increasing population resulting in urbanization as shown in Figure 1.2.

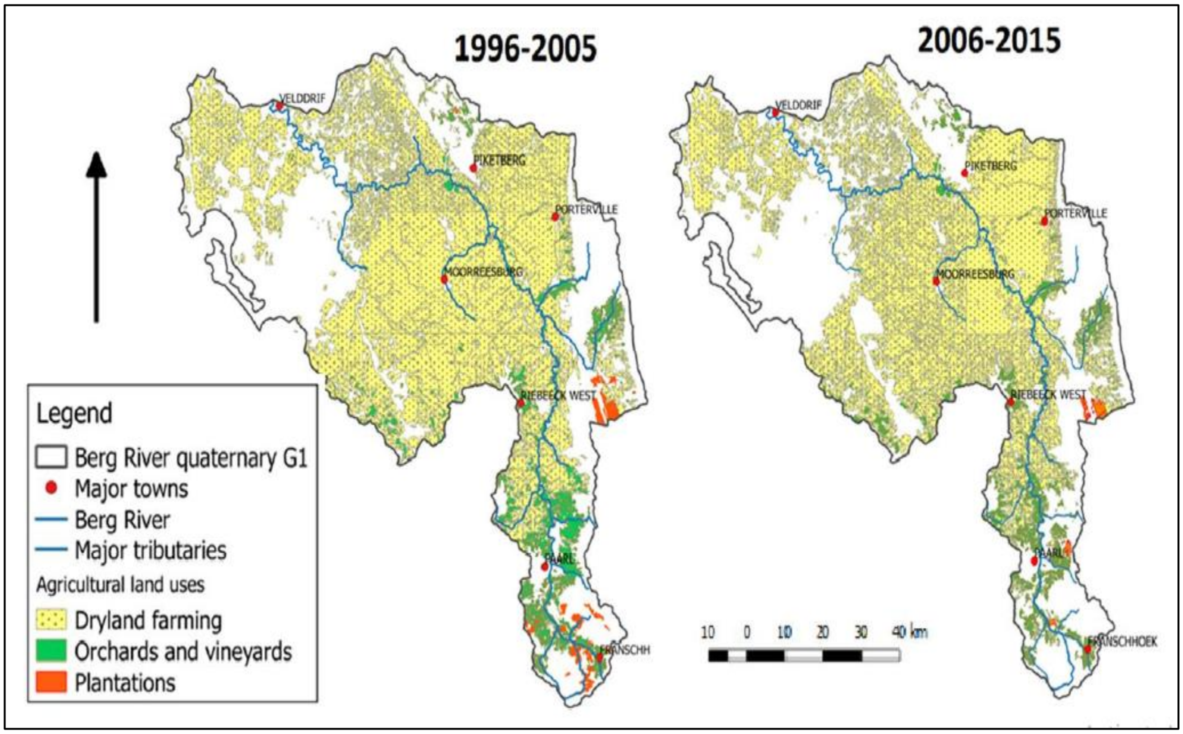

Figure 1.3: Changes in land-use of the Berg River catchment over time (Reinecke & Brown, 2018)

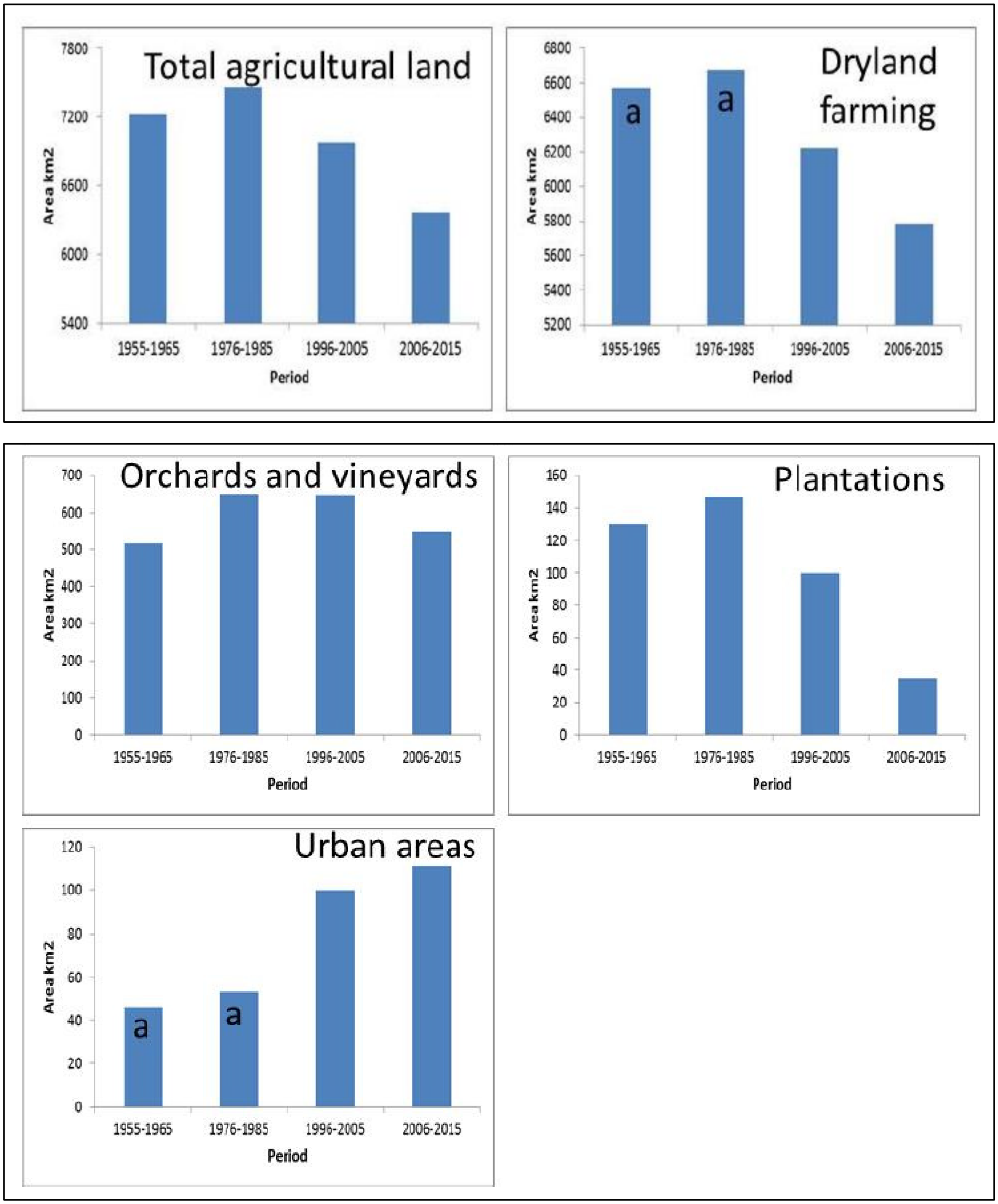

Figure 1.4: The total area of agricultural land, dryland farming, orchards and vineyards, plantations and urban areas over the Berg River catchment over time. The ‘a’ means the two periods are not different from one another ($p < 5\%$; ANOVA of least squares means) (Reinecke & Brown, 2018)

1.5 Topography, rainfall and flow regimes in the catchment

The topography of the BRC varies greatly from the headwaters to the mouth of the river, thus resulting in the great variability of the flow. According to Clark & Ractliffe (2007), the upper reaches of the Berg River are hydraulically very steep with an average bed slope of 0.67% down to Paarl. The river bed of this steep reach consists mainly of boulders and cobbles. From Paarl, the river profile flattens, with an average bed slope to the estuary of 0.045%. Madlala (2015) added that the topography ranges between minimum, mean, and maximum elevations of 213m, 238m, and 1500m above sea level respectively. The highest elevation is found at the head waters with mountainous terrain (southern part of the catchment) and flattens towards the river mouth into the Atlantic Ocean (north Most part of the catchment) as shown in Figure 1.5. It is worth note taking however that the BRC is mostly flat in terrain. The catchment receives most rainfall in winter due to its Mediterranean climate, though the precipitation distribution varies greatly in the extent of the catchment (Clark & Ractliffe, 2007). The precipitation distribution is another factor contributing to a dissimilar flow regimes in the river extent.

According to Clark & Ractliffe (2007), the BRC receives the Mean Annual Precipitation (MAP) that is usually above 1500mm in the southern parts of the catchment but decreases steadily to less than 500mm further northwards towards the mouth of the river. The MAP then drops further to below 300mm at the river mouth in Veldrift (Midgley et al., 1994). Furthermore, the Mean Annual Evaporation (MAE) in the southern and western regions of the catchment ranges from 1400mm to over 1600mm in the northeast (Görgens & Clercq, 2005). On the other hand, Midgley et al. (1994) noted that there are significant seasonal variations in monthly evaporations which fall typically between 40mm and 50mm in winter and 230mm – 250mm in the summer months. Moreover, the snow that falls on the peaks and upper slopes of the mountains during intermittent cold weather in the winter also contributes to the flow of the river (Midgley et al., 1994). In the connecting valleys, rainfall varies from 900mm to 1200mm annually, but drops to between 400mm and

500mm in the hilly plain through which the river flows most of its length, and to even less when it approaches the sea (Midgley et al., 1994).

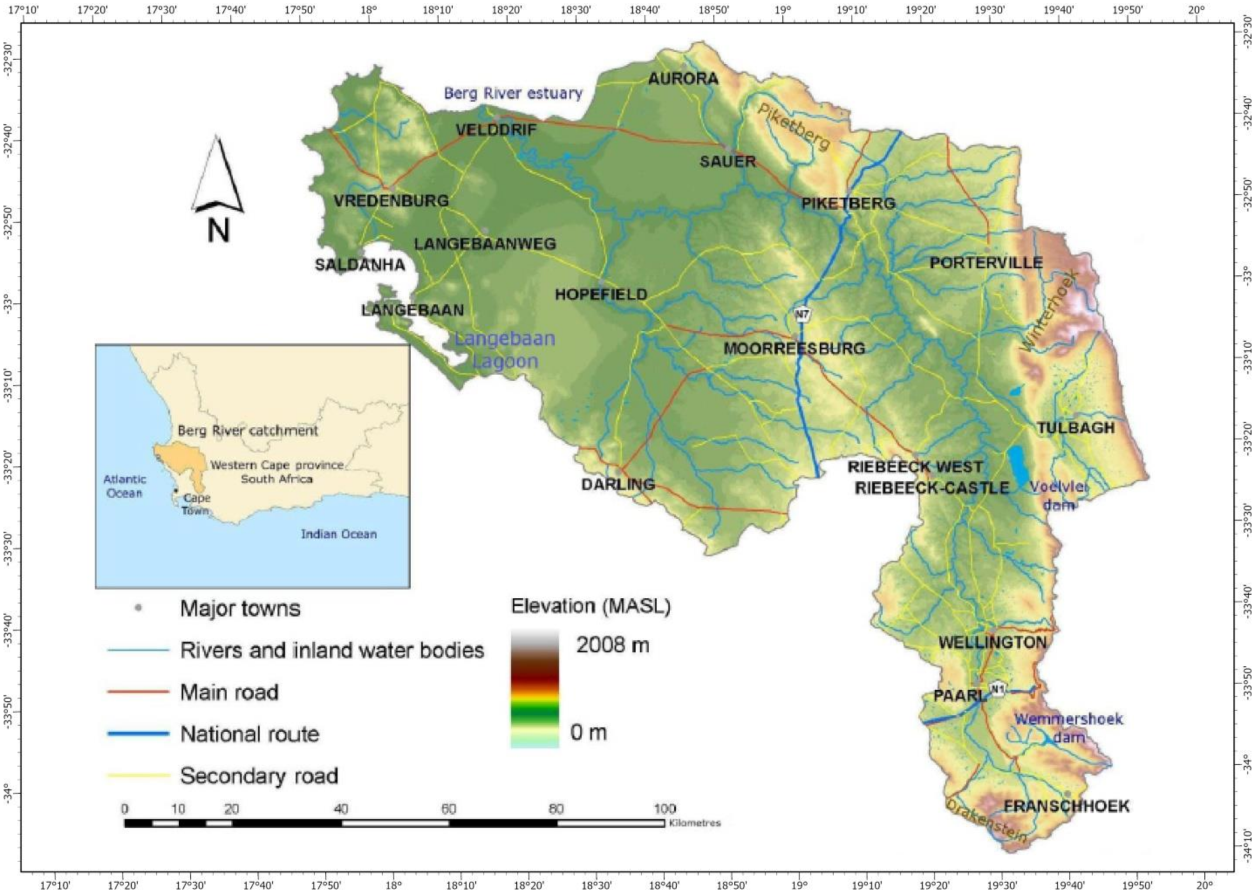

Figure 1.5: The Berg River catchment, showing major topographic features and drainage network feeding the main river (Stuckenberg, 2012)

According to Madlala (2015) the BRC has highly variable stream flow regime. The variability of the precipitation in the BRC further constitutes one of the many reasons highly variable stream flow regime. Reinecke et al. (2018) define the flow regime as the pattern and timing of high and low flows in a river. Each river’s flow regime varies from another, subject to the characteristics of its catchment and the local climate; although regional trends do emerge. The flow regime is considered as the driver of river character because, to a large extent, it determines the nature of the river channel, sediments, water quality and the life these support (Reinecke et al., 2018).

Apart from precipitation and other factors, the BRC stream flow regime is largely driven by gravity owing to the downslope from the upper to the lower reaches of the catchment. Increasing from the upper to lower reaches, natural low flows in the Berg River have varied from 0.2 to 2.0 $m^3.s^{-1}$ in the low flow period (November-April), even though not so much in recent years with Inter Basin Transfers (IBT) releases, and from 4 to 15 $m^3.s^{-1}$ in winter (May-Aug) (Clark & Ractliffe., 2007). During floods, (average daily) flows in the lower river may reach as much as 550 $m^3.s^{-1}$ and up to 80 $m^3.s^{-1}$ in the upper reaches (Clark & Ractliffe., 2007). Floods of the similar size class may last for anything from 3 to 9 days, in the upper and lower reaches. On an hourly basis, rapid flood peaks are roughly 2.5 times the magnitude of the average flood discharge for that day in the upper reaches (Clark & Ractliffe., 2007).

In Clark and Ractliffe (2007) report, it is stated that groundwater discharges to the Berg River where the depth to groundwater level is within 2.5m of the surface. It has further been reported by several authors representing a common state of groundwater discharging in the low laying fluvial plains adjacent to the Franschhoek Wetland Trust and streams in the catchment during high flow periods (Clarke & Ractliffe, 2007; Kotze et al., 2010; Ractliffe, 2007). Contrariwise, during base flow periods, higher levels of groundwater opposed to surface water introduce the hydraulic gradient required for the mobility of groundwater and discharge into surface water bodies.

Clark and Ractliffe (2007) established the direction of groundwater flow based on a developed contour map of groundwater levels in the catchment. According to the authors, groundwater was identified as flowing from areas of high elevation to those of lower elevation (along GW-SW hydraulic gradient). The contour map also shown that groundwater flows toward the center of the valley prior to flowing northwesterly toward the mouth of the river and therefore first discharges to the nearby rivers (Ractliffe, 2007). From such preceding observations, the contour map further shows areas of constant inundation, suggesting the high dependency of surface water bodies on discharges from groundwater storages.

From the above said, if it is assumed groundwater discharges into rivers in areas where the groundwater level is within 2.5m of the surface, then it is inferred that the Berg River is by and large effluent in character, meaning it receives groundwater inflow. Clark & Ractliffe (2007) added that it is only in some parts of the catchment that the river appears to be influent meaning the stream contributes surface flow to groundwater, namely:

- 14km length of river upstream of Paarl
- 7km length of river downstream of the confluence with the Doring River, and
- 20km length of river in the northern portion of the catchment, including the section of river where the Matjies River confluences with the Berg.

Contrary to the above said, Clark & Ractliffe (2007) claim that, several tributaries of the Berg River are thought to be mostly influent in character- that is, they discharge into the subsurface. The rugged topography, steep hydraulic gradients and fractured nature of the rocks suggest springs and seeps in the mountainous areas result in groundwater continually feeding the river.

1.6 Geology and soils

The geology of the BRC comprises four groups namely: a) Table Mountain Group (TMG), b) Malmesbury Group (MG), c) Cape Granite Suite (CGS) and d) Klipheuwel Group (KP). The catchment is however dominated by TMG and MG therefore the CGS and KG form a relatively small component of the total geology of the BRC (Clark and Ractliffe, 2007). The upper reaches of the BRC consists of a combination of CGS and TMG in areas between Franschhoek and Paarl. According to the Council for Geoscience (2019) (CGS) (Geology Map of South Africa), the CGS lithology includes the medium to fine grained granite and granodiorite with subordinate syenite, gabbro, diorite and quartz porphyry as shown in (Figure 1.6 read with Table 1.4 respectively). The CGS rocks formed visible outcrops, which are observable particularly in the Paarl vicinity.

The TMG nonetheless dominates the upper reaches of the catchment. There are two geologic formations making up the TMG in the BRC namely: a) Nardow Formation and b)

Peninsula Formation (Madlala, 2015:27). The Nardow Formation is made up of white coarse-fine grained, thick bedded pebbly quartz arenites, thin bedded feldsphathic and ferruginous sandstone, subordinate shale and siltstone shown in (Figure 1.6 read with Table 1.4) (CGS, 2019). Furthermore, the Peninsula Formation is made up of pebbly quartz arenites, diamictite, minor conglomerate, mudrock, siltstone and shale also shown in (Figure 1.6 read with Table 1.4 respectively) (CGS, 2019). As Madlala (2015:28) further summarised the abovementioned, the author noted that the two formations comprise primarily of chemically inert granite, quartzitic sandstones, relatively mineralized siltstones, shale, and mudstones.

Madlala (2015) further highlighted that the dominant formation in the upper reaches is the Peninsula Formation further claiming that the average thickness of the Peninsula Formation ranges between 2000-5000m. As a result, the Peninsula Formation thus constitutes the main secondary aquifer due to its vast depth (Madlala, 2015). Moreover, the Nardow Formation, Cape Granite Suite, and Franschhoek Formations occur on the east to south east of the catchment, near Franschhoek (Clark & Ractliffe, 2007 and Madlala, 2015). A layer of alluvium in the valleys covers these formations and constitutes the primary aquifer material in the catchment Clark & Ractliffe, 2007 and Madlala, 2015). Although there is great extent in the interconnectivity between the underlying fractured Peninsula Formation and alluvium, a negligible impact on groundwater levels measured has not been concluded. The abovementioned three geological formations exhibit a common characteristic, which is the high level of fracturing within them, therefore pointing the potential for large amounts of water and dissolved solutes to be transported rapidly through fracture flow.

Clark & Ractliffe (2007) also highlight that the rocks of the abovementioned formations are old and well-weathered, and typically leach very few ions. As a result, the waters of the upper Berg River and its tributaries are deemed to be naturally pure that is, they are characterized by low concentrations of TDS, including nutrients. They are also acidic, largely as a result of humic acids leached from the surrounding fynbos vegetation, which occurs in the mountains of the south-western Cape.

The TMG sandstones comprise a sequence of dissimilar formations with varying secondary porosity that play different roles in groundwater storage and circulation as aquifers, aquicludes, and aquitards (Madlala, 2015). Therefore the occurrence of mountain face seepages and spring flows is expected in this vicinity. These mountain face seepages and springs contribute greatly to the total stream flow, as expected to eventually flow into the surface water bodies, e.g. rivers. Furthermore, due to the vast fracture systems and predominance of interflow seepages, the chemistry of this water is expected to be generally being similar to that of rainwater because precipitation water has a short length of residence time in the geological formation observed during high flow periods (Clark & Ractliffe, 2007 and Madlala, 2015). It therefore becomes critical to fathom the intricacy of the lithological and hydrogeological environments based on previous studies to evaluate interaction between surface and groundwater resources in such environments to facilitate informed decision making in water resources management and use.

According to Clark & Ractliffe, (2007) the TMG sequence in the upper Berg River catchment consist of major aquifer systems owing to the highly permeability of these formations. These formations usually have substantial secondary porosity which alters the nature of groundwater flow and interactions between groundwater and surface water by introducing extra flow paths that could be used. Aquifers in these formations are highly productive and able to support large abstractions for public water supply. For this to occur, great connectivity between the fracture conduits is required.

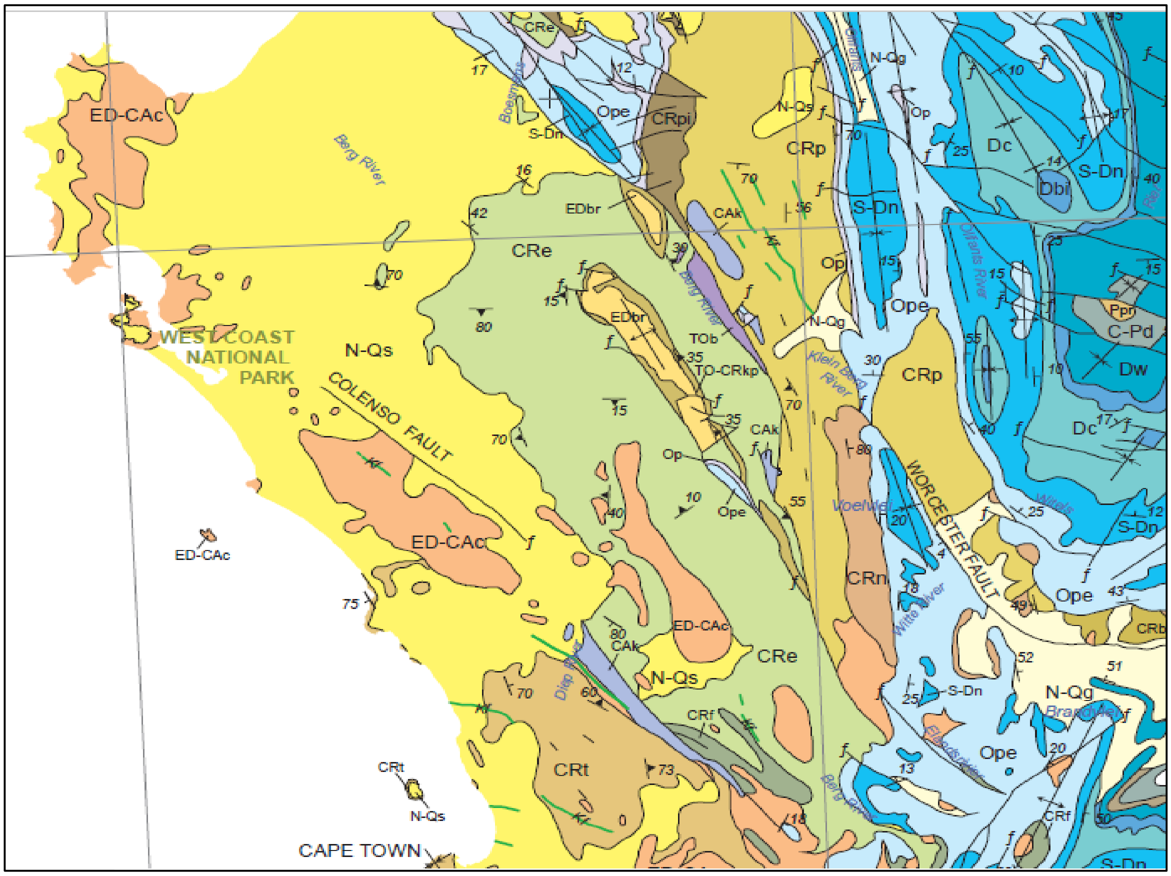

Figure 1.6: Lithology map of the BRC. Source: (CGS, 2019)

Table 1. 3 : Legend of Lithology of BRC Map sourced from: (CGS, 2019)

Code	**Group and Formation**	**Lithology**
CAk	Klipheuwel Group	Conglomerate, sandstone, mudrock and shale
Cre	Malmesbury Group, Swartland Formation, Moorreesburg	Greywacke, phyllite, schist and limestone
CRf	Table Mountain Group, Peninsula Formation, Franschhoek	Quartzite, conglomerate and slate

CRp	Malmesbury Group, Boland Formation, Poterville	Phyllite shale, greywacke, limestone and arenite
Crpi	Malmesbury Group, Boland Formation, Piketburg	Phyllitic shale, greywacke and subordinate limestone
ED-CAc	Cape Granite Suite, Paarl	Porphyritic, medium-fine grained granite and granodiorite with subordinate syenite, gabbro, diorite and quartz porphyry
N-Qs	Malmesbury Group, downstream of Paarl	Quartzose sand, pelletal phosphorite, gravel, sandy-silt grey-black carbonaceous kaolinitic clay, peat, shelly limestone and sandstone, shelly sand and (aeolian) calcarenite, coquinite, light grey-reddish sandy soil, loamy sand
Ope	Table Mountain Group, Peninsula Formation, Franschhoek-Paarl	Pebbly quartz arenite, diamictite, minor conglomerate, mudrock, siltstone and shale
S-Dn	Table Mountain Group, Nardouw Formation, Franschhoek-Paarl	White coarse-fine grained thick bedded pebbly quartz arenite, thin bedded feldspathic and ferruginous sandstone, subordinate shale and siltstone
TOb	Malmesbury Group, Boland Formation	greenstone, dolomite, chert, quartz-serecite and graphite schist
TO-CRkp	Malmesbury Group, Swartland Formation	Quartz-serecite, chlorite, schist and phyllite

Fracture networks upscale the spatial extent upon which surface and groundwater can interact and increases the possibility of interaction. Fractures also behave as conduits for water and any contamination thus may be primarily important in the connectivity between surface and groundwater. Large amounts of water are able to flow within connected fracture networks, while the sandstones of the TMG (Peninsula formation) are chemically inert, rendering the chemistry of water flowing through them fairly unchanged. The exceptions are evident were formations change from sandstone to shale-siltstone of the Malmesbury Group (MG), which have decreased permeability and increase the level of mineralization of the water. The Berg River water quality is noticed to deteriorate with distance downstream, with leading negative influences from human settlements and agricultural activities (De Villiers, 2007; Paulse, et al., 2007).

The MG is the most dominating group of rocks in the middle-lower areas of the catchment such as Darling, Moorreesburg, Piketburg, and Porterville as well as the areas towards the river mouth (Clark & Ractliffe, 2007). Kisters (2016) claimed that the MG originates from the CGS. Kisters (2016) further elaborate that the composition, structures, isotope characteristics and age of deep-crustal, high-grade metamorphic wall rock xenoliths in the granites are similar to that of the MG exposed at surface resulting in clayey soils of the MG as a result of weathering. Moreover, Kisters (2016) stated that rocks of the MG are largely marine sediments, shales and greywackes that were deposited in a near-shore to deep-water environment.

Structurally, rocks of the Malmesbury Group are folded into northerly to northwest-trending, doubly plunging and more or less vertical or southwest-verging folds (Kisters, 2016). The folds are present and visible largely throughout the Western Saldania Belt and are classified F2 folds (Kisters, 2016). An earlier fold generation (F1 folds) is preserved in the cores of regional scale F2 antiforms in the central parts of the western Saldania Belt that uncover the structurally deeper parts of the Malmesbury Group (Kisters, 2016). These F1 folds are mainly recumbent, isoclinal, intrafolial folds that pervasively refold and overprint original bedding features. Kisters (2016) further claim that most regional studies focus on the presence and significance of the regional-scale, northwest-trending strike-slip faults of the Colenso and Piketberg-Wellington faults (Figure 1.7). The faults stretches up to numerous kilometer-wide fault zones are generally thought to disconnect three structurally and lithologically distinct formations comprising the southwestern Tygerberg, central Swartland and northeastern Boland terranes as shown in (Figure 1.7) although southwestern Tygerberg Formation does not fall within the present study area.

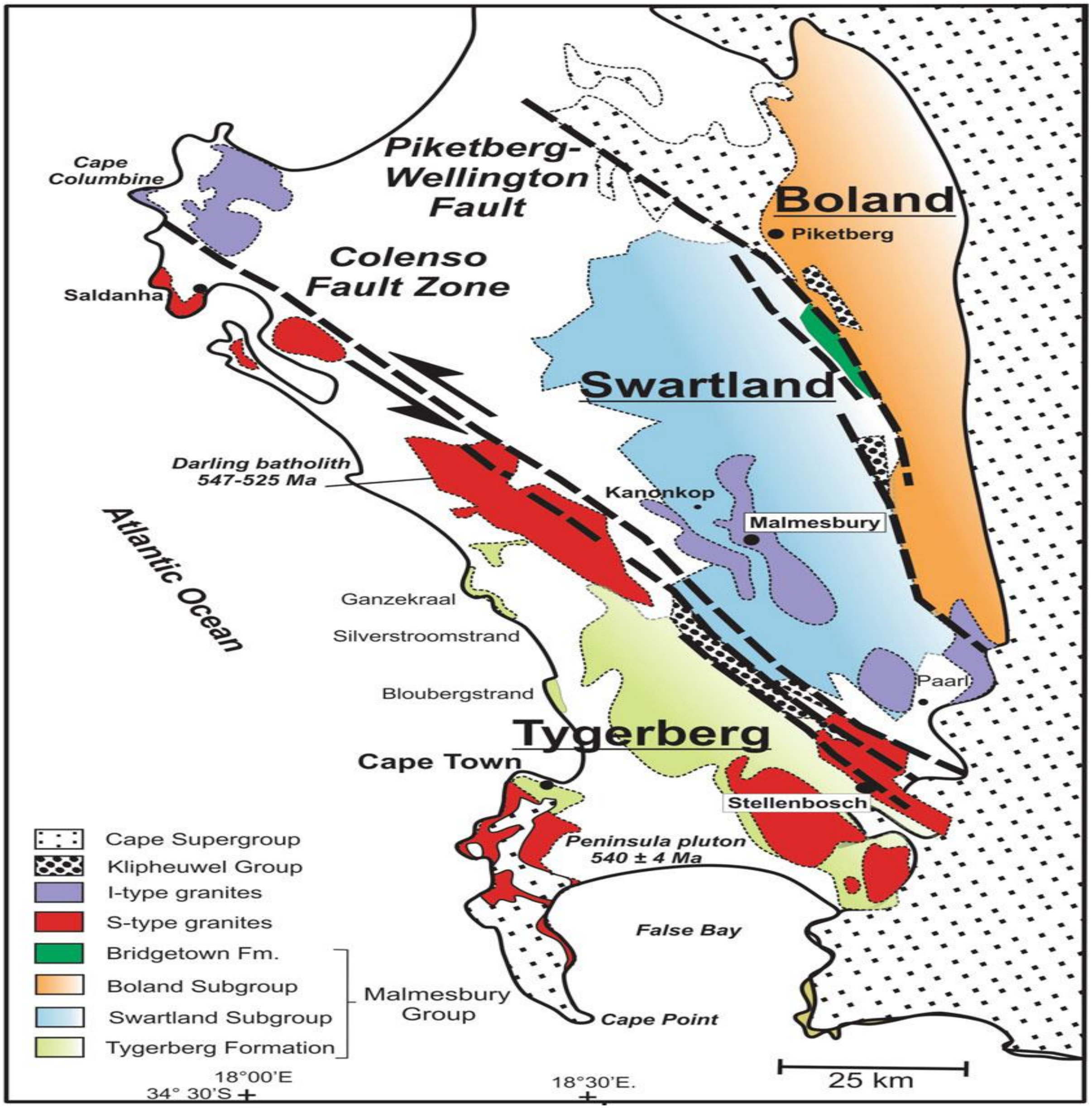

Figure 1.7: Geological map of the western Saldania Belt in the Western Cape. Source: (Kisters, 2016)

The Swartland Formation is the dominant domain compared to Boland Formation within the Malmesbury Group. According to Kisters & Belcher (2018) the Swartland is interpreted to be separated from the Boland terrane by the Piketberg-Wellington fault. Therefore, Boland Formation is found east of Swartland in areas such as Piketberg, Porterville and Tulbagh and comprises units such as greenstone, dolomite, chert, quartz-serecite and graphite schist (CGS, 2019 and Kisters, 2016). Swartland Formation on the other hand is found on the west of Boland Formation in areas such as Moorreesburg, Malmesbury, Hopefield and the areas in the lower reaches towards the river mouth. The Swartland Formation consists of quartz-serecite, chlorite, schist and phyllite (CGS, 2019).

There have been numerous claims that groundwater quality in the Berg River Catchment is generally quite poor in the middle-lower reaches of the catchment owing to the geologic setting of the MG (Cullis et al., 2019, Bugan, 2014, Albhaisi et al., 2013, Clark & Ractliffe, 2007, De Villiers, 2007:2-6, Nitsche et al., 2006). Clark & Ractliffe added that groundwater quality is controlled by, amongst other factors, lithology, residence time and rainfall. Aquifers consist of rocks of the MG generally yield poor quality groundwater with a NaCl character and an EC fluctuating between 100 and 1 000 mS/m. Very poor quality groundwater is encountered in the drier western extremities of the Malmesbury Group Aquifer (Albhaisi et al., 2013).

1.7 Geohydrology

The geohydrology of the BRC is determined by the geological groups mentioned above. The four geologic groups consist of five distinct aquifer types that occur in the Berg River Catchment namely: the Table Mountain Group Aquifer (TMGA), the Cape Granite Suite Aquifer (CGSA), the Malmesbury Group Aquifer (MGA), the Klipheuwel Group Aquifer (KGA) and Primary Aquifers (PA) comprising unconsolidated alluvial deposits and reworked marine deposits (Ractliffe, 2007). On a regional scale, Meyer (2001) described the TMGA, MGA and KGA as fractured aquifers, the PA as an intergranular aquifer and the CGSA as intergranular and fractured aquifers. Furthermore, Ractliffe (2007) further highlighted that MGA is the dominant secondary aquifer system and underlies most of the area in the central and lower catchment. On the other hand, the TMGA predominantly occurs in the upper catchment and along the eastern and northern fringes of the catchment in which the Berg River Dam exist (Meyer, 2001 and Ractliffe, 2007). The CGSA and KGA form a relatively small component of the total groundwater system in the catchment (Ractliffe, 2007).

According to Meyer (2001), secondary aquifers in the BRC are those which owe their water-bearing properties to weathering, fracturing and faulting processes. Although it could be assumed that fractured rocks yield appreciable quantities of water, it is however worth note taking that the clay nature of most of the rocks such as the MGA and poor groundwater quality limit the exploitation potential of these aquifers (Meyer, 2001, DWAF, 2007 and Ractliffe, 2007). Groundwater in the lower catchment area occurs in two distinct primary aquifers, namely the upper unconfined aquifer system comprising sediments of the Bredasdorp Formation and the lower confined aquifer in the Elandsfontyn Formation (Timmerman, 1985); Wright & Weaver, 1994 and Woodford, 2003). While the overlying Bredasdorp Formation aquifer has a greater extent, poor water quality results in it having limited potential for development for bulk water supply purposes. The Langebaan Road Aquifer is currently being tested as a source of water for the towns to the northwest of the catchment (DWAF, 2007).

1.8 Selected hydrogeochemical parameters

The present study focuses on hydrogeochemical investigation of the surface and groundwater interaction particularly the role that geology and soils play on water chemistry in the BRC. The study therefore employed major cat-ions and an-ions and electrical conductivity (EC) to identify the hydrogeochemical characteristics, water chemistry changes and trends in surface and groundwater over the years as well as to evaluate its suitability for drinking which are tabulated in (Table 1.4) below. Furthermore, the hydrogeochemical parameters were measured against the SANS 241-1 2015 as well as the Domestic Water Guidelines Vol 1 of 1996 of the DWS as some of them are not listed in the SANS 241-1 2015. Table 1.4 below present the water quality limits. The limits are classified from low to significant with different colors as per the potential to harm human health.

*Parameters were measured against the SANS 241-1 2015 are in bold format.

*Parameters were measured against Domestic Water Guidelines Vol 1 of 1996 are not in bold format.

*All parameters were measured in Mg/L except EC which was measured in mS/m.

Table 1.4: Hydrogeochemical parameters and Water quality limits from SANS 241-1 2015 and Domestic Water Guidelines Vol 1 of 1996

Variable	**Low**	**Moderate**	**High**	**Significant**
Ca^{2+}	0-32	32-80	≥80	N/A
Cl^{-1}	0-100	**≤300**	300-1200	≥1200
Mg^{2+}	0-70	70-100	100-400	≥400
EC	0-70	**≤170**	170-450	≥450
Na^{+}	0-200	**≤200**	200-1000	≥1000
NO^{-3}+NO^{-2}	≤1	≤1	**≥1**	1≥20
K^{+}	0-5	50-100	100-400	≥400
SO^{-4}	0-250	**≤250**	**≤500**	≥500
Total Alkalinity (TAL) (HCO^{-3})	0-100	100-200	200-300	≥300

*Low- No negative health impacts

*Moderate- Possibility to impact the aesthetic

*High- Possibility to negatively impact sensitive people, elderly and infants

*Significant- Causes adverse health on everyone

1.9 Statement of research problem

The interaction of surface water and groundwater to this day remains one that is complex and poorly understood as surface and groundwater were previously considered as separate components in the application of water resource management. The lack of understanding therefore continues to create gaps in determining important information on the quantity and quality of groundwater in particular (Winter et al., 1998). The complexities in determining the interactions between surface water and groundwater has thus led to surface water receiving much attention as it is readily available and accessible to study as opposed to groundwater (Winter et al., 1998; Tanner, 2013; Abiye et al., 2015 and Madlala, 2015).

Furthermore, among many of the important issues that can potentially be missed, is the issue of how the natural setting (geology and soils) influence the chemistry and the latter quality of water. Lintern et al. (2017) stated that geology and soils play a vital role in water chemistry across borders. Therefore, the understanding of chemical reactions related to water and geologic setting and soils are of ultimate importance for a catchment that is used for water supply. A case study can be drawn from “Impact of acid mine drainage in South Africa” authored by McCarthy (2011). The study by McCarthy (2011) was driven mainly by concern arising from the decanting of contaminated water from the old gold mines in the Krugersdorp area into the Cradle of Humankind. The research focused primarily on the immediate problems arising from gold mining and in particular on the defunct mines in the Western Basin (Krugersdorp area), the Central Basin (Roodepoort to Boksburg) and the Eastern Basin (Brakpan, Springs and Nigel area).

McCarty (2011) study detailed that the process of mining involves extracting the gold-bearing conglomerate layer and transporting it to the surface where it is crushed and the gold is extracted. After extraction of the gold, the crushed rock is deposited on waste heaps known as tailings dumps. Rainwater falling on the dumps oxidises the pyrite, forming sulphuric acid which percolates through the dumps, dissolving heavy metals (including uranium) in transit, eventually joins the local groundwater as a pollution plume. This polluted water ultimately emerges on surface in the streams draining the areas around the dumps. Streams draining the tailings dumps are therefore typically acidic and have high sulphate and heavy metal concentrations. Once mining operations cease, pumping also ceases and the void created by mining slowly fills with water. This water originates as rain and contains dissolved oxygen. In its slow passage through the old workings it becomes acidic and enriched in heavy metals. Once the mine void fills completely, decant of this polluted water commences. Decanting will occur from the lowest lying opening to the old workings, as is currently the case affecting the Blesbokspruit in the Springs area and Klip Rivier in the Witwatersrand area.

This study concluded that AMD related to gold mining is especially affecting not only the groundwater in those mining areas but the Vaal and Olifants River systems we all through decants. These are not the only areas in the country afflicted by this malady, but because of the particular local conditions, the problems in the Olifants and especially the Vaal River basins are huge by comparison and pose a serious threat to future generations of South Africans.

Moreover, in South Africa, much of the water used is obtained from surface water bodies like rivers, springs and earth dams. The dynamics of surface and groundwater chemical transfers has not been thoroughly studied and well understood in the country. Such a case is also observable from the Berg River catchment (BRC) wherein surface water quality have been severely studied (Ractliffe, 2007), while on the other hand groundwater chemistry and quality in relation to the natural setting remains questionable. This study will therefore provide an investigation of the interactions of surface and groundwater using hydrochemical and geological information in the BRC, to determine the extent to which natural setting influences the chemistry of surface and groundwater.

1.10 Research Questions

- What aspects of geology and soils control the water chemistry in the catchment?
- Does the chemical composition of water in the BRC reflects the chemical makeup of geology and soils in the catchment?
- What geochemical processes control or play a role in water chemistry in BRC?

1.11 Aims and Objectives

The main aim of the study was to understand the interaction between surface and groundwater in the Berg River catchment. For this purpose, the objectives of the study are:

- To investigate the role that geology and soils play on water chemistry in the BRC.
- To identify BRC surface and groundwater chemical trends.
- To identify the geochemical processes controlling surface and groundwater chemistry in BRC.

1.12 Significance of the study

South Africa is a water scarce country in which the scarcity is exacerbated by pollution. Western Cape Province alone has been hit hard by drought. As such, the exploration of groundwater seems to be the immediate solution to numerous people in the province and the country in general to meet the daily demands as water is a basic need. It is therefore important to investigate what impacts surface and groundwater have on each other in terms of chemical exchange prior to exploration so as to provide good quality water to water users.

This study is therefore imperative in that it gives better alternative method (the use of geological information and hydrochemical information) for water quality management not only in the Berg River catchment, but the entire South African water catchments to safeguard both surface and groundwater from pollution. Mapping of chemical parameter migration will therefore inform the catchment managers and users on which hydrological units (aquifers in particular) are next target of pollution. With this information, catchment managers can therefor make means to prevent pollutants from reaching the aquifers.

Furthermore, this study will contribute significantly to National Water Resource Strategy (NWRS) well as Department of Water and Sanitation which aims to ensure that water resources in the country are sustainable and there is access to safe and clean water and eradication of pollution. Moreover, the study will stimulate hydrological research and contribute more to environmental management at large.

1.13 Delineation

This study will investigate the chemical parameter migration between surface water and groundwater in the BRC, Western Cape. The study will make use of geological information and hydrochemical information from geological literatures as well as the Department of Water and Sanitation National Water Monitoring Database found on this website http://www.dwa.gov.za/iwqs/wms/data/000key.asp. The study will look at chemical contamination trends, transportation and interaction points (recharge and discharge).

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Safe drinking water is a necessity for humans and other living organisms. Khatri & Tyagi (2015) claim that the availability of safe drinking water has been improved in the last few decades however; about one billion people still do not have access to safe drinking water due to various reasons. Industrial activities in particular are known to have capability to alter water quality when discharged into the receiving environment, consequently enhancing chemical contamination in water bodies. Bosman (2009); Saayman (2012) and Western Cape Government (2012) emphasized that industrial activities are the reasons why accessibility of safe drinking water to be the rarest thing in Southern Africa. That said, surface water is found to have been more prone to biological, physical and chemical contamination than groundwater.

Although studies regarding water quality have been well documented, the interaction of surface and groundwater with regard to their impacts on water quality, however remain a complex and poorly understood issue in South Africa due to vastly relying on surface water. The migration of chemicals and minerals between surface and groundwater are at times overlooked due the lack of interest and correct technology for such studies (Sophocleous, 2002). One in particular is the issue of the human and geologic influences of water chemistry in the BRC (Bosman, 2009).

The BRC is one of many catchments in the country that have the record of excessive nitrates as well as salts (NaCl) present in water (reference). Sophocleous, 2002) and Bosman (2009) however, highlighted that excessive nitrates and salts are not very common in groundwater but indicate anthropogenic activities and surface and groundwater exchanging constituents. Consequently, salts such as Na and Cl are found in both surface and groundwater although their origin in surface water might be from various sources. Such studies are however not well documented in the country and as such, this study will furthermore make use of hydrochemistry methods to investigate such interchanges migration.

2.2 Previous studies in the BRC

Interaction and interchange of constituents in surface and groundwater systems have been successfully studied across the globe to establish the impacts such dynamics have on the water quality and quantity. Many of the literature outcomes established the impact that the geological setting has on the overall quality of water in a catchment (Olson, 2012, Yang, 2018, Al-Agha and El-Nakhal, 2004 & Narany et al., 2014). This occurs in many ways described below by (Brunner et al., 2011):

- Chemical weathering of the bedrock which influences the groundwater quality
- The structural geology which have an influence by means of primary and secondary porosity and permeability.

In the BRC however, more focus was placed on studying the quality of surface water as and very minimal focus was placed on studying groundwater. In addition, the previous studies were sparked due to concerns that water users expressed about certain water quality indicators being unacceptable. Nitsche et al. (2006) highlighted that concerns of salinity increases in the Berg River main stem and eutrophication at certain areas of the catchment such as the Misverstand weir have resulted in various research investigations in the catchment.

Nitsche et al. (2006) further highlighted the study conducted in the 1950s authored by Harrison & Elsworth (DWAF, 1993). The study was fundamentally conducted to investigate the degree of pollution in the Berg River. Fourie & Steer (cited by DWAF, 1993) and Fourie & Görgens (1997) investigated the mineralization of the river. It was found that the salinity increases in the Berg River could be due to an increasing irrigation along the river extent. Nitsche et al. (2006) further added that the parameters of concern in the catchment were:

- pH

- Salinity (TDS and EC)
- Phosphates
- Temperature
- Oxygen

Nitsche et al. (2006) in the study which was investigating the application of hydrodynamic river flow and reservoir water quality models to the berg river system concluded that salinity is only a concern in the lower reaches of the catchment. Bugan (2014) in his study which was aimed at studying the characteristics and causes of spatial and temporal dynamics of water cycle components and inorganic salt fluxes in the Sandspruit catchment (tributary of the Berg River) also concluded that salinity is a major concern only in the lower reaches of the BRC. Naicker (2012), Bugan (2014) and Görgens & Clercq (2005) further claimed that the salinity in the BRC is a result of the weathering of the Malmesbury bedrock contrary to the Harrison & Elsworth (1958) study which concluded that the salinity was due to irrigation.

Another water quality concern in the BRC is the trophic state on certain parts of the catchment. According to De Villiers (2007) the inorganic nitrogen and phosphates levels also increases downstream in response to anthropogenic inputs. In De Villiers (2007) findings, the author highlighted that the Berg River monitoring stations experience episodic hypertrophic conditions as DWAF (2002) classification where the long term median value indicated an almost 10 folds downstream increase in NO_3^-+NO_2^- as well as PO_4^{3-}. De Villiers (2007) further highlighted that the most problematic areas are middle to lower reaches of the catchment particularly between Paarl and Hermon displayed long term NO_3^-+NO_2^- values exceeding international standards for aquatic and plant life.

The NO_3^-+NO_2^- levels further demonstrated well-defined seasonal changes and that the amplitude of this seasonal cycle has remained fairly constant since the 1980s at all stations except the monitoring station at Hermon as well as Drieheuwels situated a little upstream of Misverstand in the middle Berg (De Villiers, 2007). Several authors further claimed that the two most likely anthropogenic sources of nutrients in the Berg River are agricultural runoff and effluent from overloaded municipal sewage works and unsewered communities (De Villiers, 2007:2-6).

Moreover, the trend has been established where an increase due to non-point sources such as agricultural runoff occur in high rainfall season (winter season) whereas point sources increases occur during the low rainfall season (spring-autumn) (De Villiers, 2007). However, the overloading of the Wastewater Treatment Works during high runoff seasons or flooding of informal settlements during the winter months storm events may have also resulted in nutrient enrichment from the point sources (De Villiers, 2007).

Contrary to the previous studies which were mostly focused on surface water quality, the current study is a combination of surface and groundwater investigations and their interactions with respect to transfer of constituents and their water quality impact on both surface and groundwater systems.

2.3 Water quality status of the Berg River Catchment

2.3.1 Nitrate Pollution in the BRC

Nitrates amongst other chemicals are used as water quality indicators in many parts of the world where values exceeding 10mg/L of nitrates in drinking water is regarded as nitrate contamination (Mgese, 2010). That said, nitrate pollution refers to high concentrations of nitrates in water exceeding the guidelines limit and may therefore result in adverse health impacts (Deksissa et al., 2004 and Mgese, 2010). Ribbe et al. (2008) added that nitrates enter the surface water directly as a result of runoff from nitrate containing fertilizers from agricultural activities. They furthermore enter the surface water by means of discharges from waste water treatment works, industries, animal faeces and or raw sewage from inappropriate sanitation in informal settlements (Tredoux & Talma, 2006). The most negligible source of nitrates in South Africa is mining, particularly open pit mines. A study carried out in several mines in the Limpopo Province, indicated that open pit mines are major contributors of excessive nitrates in the ground water system in the province, although it has always been assumed that elevated nitrates were a result of improper sanitation (Bosman, 2009).

Having said that, human health is a typical standard used for testing nitrate toxicity in South African Drinking Water Standard quality guideline for domestic use which is set at 6mg/L as inorganic nitrogen-NO_3N, which seems to be lenient as compared to Europe which has set nitrates standards to 5.5mg/L for drinking water (Tredoux & Talma, 2006 and Bosman, 2009). Over and above, both regions are still within the international nitrate standards set at 10mg/L by World Health Organization (WHO, 2016).

These standards were set so as to avoid the adverse health impacts that are the consequence of excessive nitrates in drinking water. Bosman (2009) highlighted that nitrate readily transforms in the gastrointestinal tract to nitrite as an effect of bacterial reduction. Nitrite upon absorption, syndicates with haemoglobin which is the oxygen transporting red blood pigment to form methaemoglobin, rendering the blood incapable of carrying oxygen. The abovementioned process constitute the formation of methaemoglobinanemia disease or commonly known as the blue baby syndrome (Bosman, 2009).

In addition, Bosman (2009) stated that values between 6 and 20mg/L could lead to methaemaglobinanemia in infants, while values above 20mg/L will sure cause methaemaglobinanemia in children, and mucous membrane irritations in adults. Moreover, values above 51mg/L are fatal to livestock. Signs and symptoms of methemoglobinanemia include shortness of breath, cyanosis, mental status changes, headache, fatigue, exercise intolerance, dizziness and loss of consciousness (Bosman, 2009). Metabolically, nitrates may also react with amines and amides, commonly found in food such as meat to form nitrosamines, which are known carcinogens (cancer causing agents), and which can lead to especially stomach cancer (South African Water Quality Guidelines, 1996). Other risks related with infant methaemoglobinaemia are augmented by bacterial pollution, malnutrition, and weak health, e.g. immune compromised individuals. The daring parts of this illness are symptoms which are similar to common illnesses such as influenza which could be the very reason why methaemaglobinaemia is often negligible and not notifiable in Southern Africa (Tredoux & Talma, 2006).

Although no statistics have been presented on morbidity and mortality, it is known from the literature that infant methaemoglobinaemia does occur in Southern Africa (Super *et al*., 1981; Hesseling *et al*., 1991 and Tredoux *et al*., 2005). Correspondingly, no concurrent statistics are available on the loss of livestock due to nitrate poisoning; however, there has been a speculation of considerable losses of livestock incurred over the past three decades that may be due to nitrate poisoning (Marais, 1991, Tredoux *et al*., 2005). The overall lack of recorded information on the occurrence of infant methaemoglobinaemia and livestock losses in Southern Africa thus tends to obscure the seriousness of nitrate pollution.

Moreover, elevated nitrate levels together combined with phosphates cause eutrophication in water resources (US EPA, 1998). This is the phenomenon whereby the presence of both nitrates and phosphates exacerbate dense growth of plants, algae in particular (US EPA, 1998). Eutrophication is a global water issue as the dense plants covers the top of surface water body such that sunlight cannot penetrate into the water. Consequently, plants at the bottom of the water body cannot photosynthesize due to lack of sunlight and eventually die off (Chislock *et al*., 2013). The whole process has the potential to collapse the entire food web in the water body (Chislock *et al*, 2013). Although eutrophication is rare in moving water, Mgese (2010) stated that rivers such as Berg River have been hit by this phenomenon. Mgese (2010) further added that Berg River also reached its trophic status between Paarl and Mbekweni informal settlement.

The aforesaid clearly indicate the importance of conducting studies to trace and monitor nitrate sources as well as its movement in both surface and groundwater systems in South Africa. Having said that, it is worth note taking that the study of nitrate concentrations in South Africa is not novel but it has been constrained by obtainable data, and methodologies used to acquire nitrate data were not very advanced particularly in the groundwater (Tredoux & Talmas, 2006). Such constraints steered nitrates to become a negligible subject thereof.

2.3.1.1 Sources of pollution

Water in its pure form is deemed fresh and safe from consumption and other uses. Water is therefore deemed unsafe for use when acted upon by various activities which may be both natural and anthropogenic processes. Some anthropogenic uses of water such as agricultural production (feedlots) industrial production, mining, power generation and forestry practices have a huge potential to cause deterioration in the water quality and ultimately the water quantity (Khatri & Tyagi, 2015).

Water quality is measured by assessing the physicochemical and biological properties of water against a set of standards. Water quality measure is used to determine whether water is suitable for consumption or safe for the environment (Khatri & Tyagi, 2015). Furthermore, water quality is determined by the analysis if water samples collected in both surface and groundwater periodically at monitoring stations. The results of water quality monitoring are crucial in determining the special and temporal trends in surface and groundwater (Khatri & Tyagi, 2015).

Water quality results also reveal various types of possible contaminants and or environments in which the water have been exposed to. The various possible sources of water pollution are illustrated on the below flow chart.

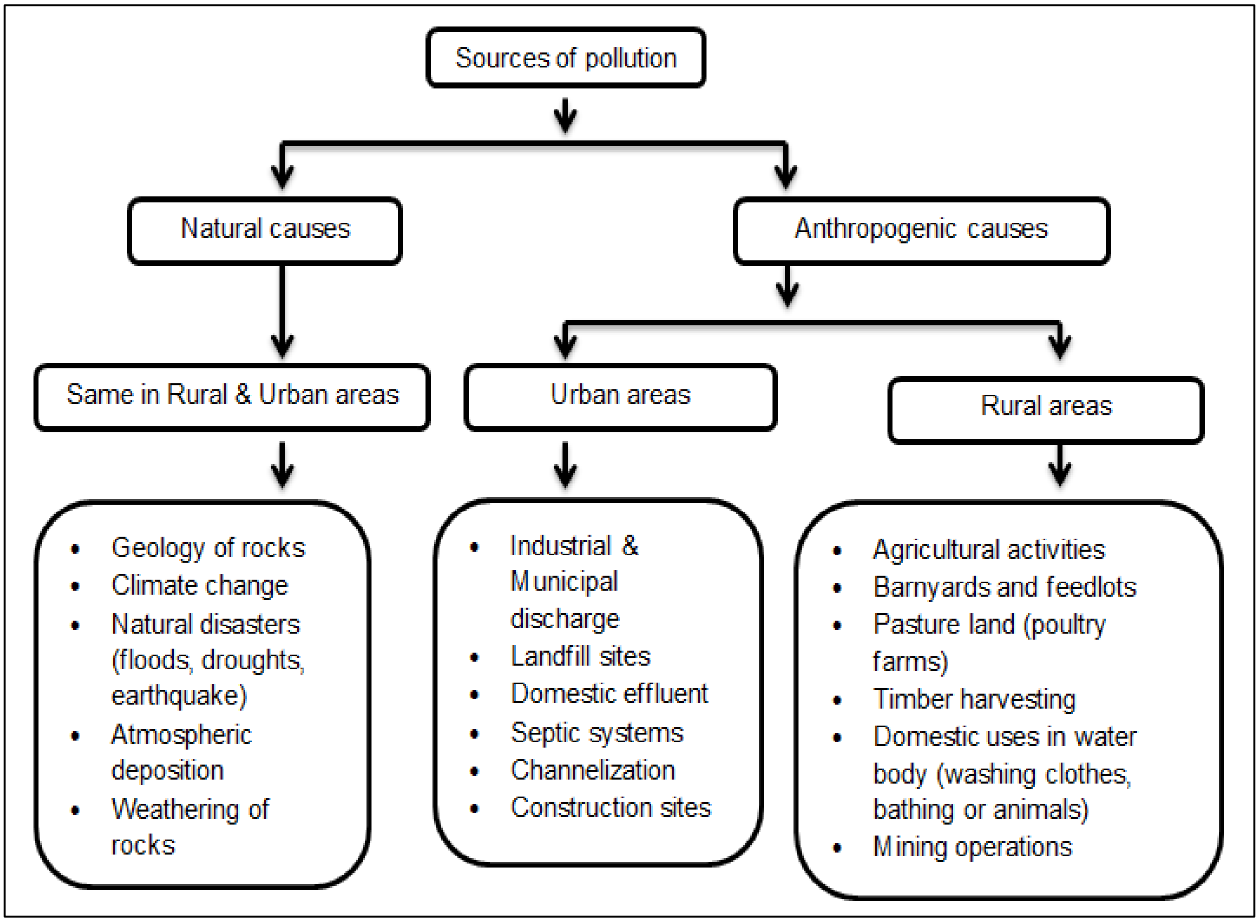

Figure 2.1: Flow chart showing natural and anthropogenic sources of water pollution in rural and urban areas. Source: (Khatri & Tyagi, 2015)

2.4 Surface and Groundwater interaction

Water is a scarce commodity in certain parts of the world while in others water occurs in abundance. Although in certain parts of the world water is abundant, it is important to fathom that there is only a finite quantity of water on Earth (Ohio Department of Natural Resources, 1997). Of that quantity, only limited percentages is suitable for anthropogenic activities and other living organisms. The ocean consists of 98% while the remaining 2 percent constitute fresh water found mostly in the atmosphere and locked up in glaciers. Furthermore, drinkable water from surface water and ground water only accounts for less than 2% of the planet's fresh water reserves (Ohio Department of Natural Resources, 1997). Therefore, since humans and other living organisms have limited amount of consumable water, it is crucial to study and comprehend the mechanisms and interactions of how and where water flows.

The interaction of surface and groundwater is one of the main processes in which water in the two components connect in the Earth’s hydrosphere (Cherepansky et al., 2009 and Albhaisi *et al.,* 2013). As such, surface and groundwater are closely interconnected through the hydrologic cycle, a global phenomenon in which water continuously moves through an intricate system. While the interactions of surface and groundwater are fairly studied across the world, Sophocleous (2002) stated that the deeper understanding of the dynamics still remains complex. Sophocleous (2002) highlighted that in order to fathom the process one needs to have an understanding of the geological background, hydrogeology, climate, landscape and biotic factors just to mention a few.

The above factors thus affect the quantity, quality and the mobility of water between surface and groundwater in a form of recharge and discharge (Cherepansky et al., 2009). The two main processes include: filtration (recharge) of surface water out of lakes, rivers, and raised bogs into rocks of the upper geological strata, and filtration (discharge) of ground water into river beds, lake basins, lowland bogs and marine hollows, forming the so called underground component of global circulation (Cherepansky et al., 2009). Furthermore, Conrad et al. (2004) added that groundwater discharge manifest itself by means of springs, hydraulic connection between aquifer and river or lake and by confined groundwater moving by complicated sub-vertical upward filtration, through relatively poorly permeable rocks. Others include base flow (discussed later in the chapter) and interflow into the streams; however, these are rare occurrences.

In addition, the geology of the area, climate and landforms not only impact the recharge and discharge in the process of interaction but also impacts on the materials surface and groundwater exchange. That said, regions with considerable precipitation, effortlessly permeable soil, a low density of vegetative cover, and little relief are favourable for ground water recharge (Albhaisi *et al.,* 2013). These areas must be regularly monitored since any pollutant discharged can be promptly transferred to the ground water aquifer (Ohio

Department of Natural Resources, 1997 and Albhaisi *et al.,* 2013). Conrad et al. (2004) further indicated that once the contaminant reaches the aquifer, it moves with the ground water and ultimately settles in surface water. Although soils and rocks may act as a limited filter for contaminants, once these natural filters are overwhelmed with excessive concentrations of pollutants, discharge to surface water is inescapable (Sophocleous, 2002).

Despite many natural factors playing a role in the interaction of surface and groundwater, DWAF (2007) and Mgese (2010) stated that some anthropogenic acts manipulate groundwater recharge by means of irrigation which is capable of altering the chemical makeup of groundwater. This sort of anthropogenic activity is the recharging of groundwater using the existing surface water which is regularly for the purpose of groundwater usage on crops for lower rainfall events (DWAF, 2007 and Albhaisi *et al.,* 2013). Furthermore, irrigation constitutes a common practice in the BRC where the irrigation return flows are used during low rainfall seasons. As such Görgens & Clercq (2005) and DWAF (2007) noted that Voelvlei, Theewaterskloof, Wemmershoek and Misverstand Dams not only supply water for domestic use but also supply irrigation water to 8 irrigation boards in the catchment along with their various irrigation schemes.

Noting that the Berg River's water quality is poor, it is therefore concerning that the very same compromised quality of water is injected into groundwater for later uses. Sophocleous (2002) highlighted that the interaction of surface and groundwater is both ways, in which contaminants can also travel back to surface by means of groundwater recharges and consequently the cycle of contaminants or pollutants will be a continuous process in the BRC. Görgens & Clercq (2005) reported that salinity and phosphates levels are rapidly increasing in surface water in the BRC as a result of increased irrigation return flows in low rainfall seasons.

2.4.1 Mechanism of GW-SW

Winter et al. (1999) and Chen et al. (2013) identified three basic ways in which stream/river systems can interact with the groundwater as shown in (Figure 2.2):

- Streams gain water from inflow of ground water through the streambed and it is therefore regarded as a gaining stream. For this condition to exist the stream should be hydraulically connected to the groundwater and the stream stage should also be at lower elevation in comparison to the aquifer water levels.
- Streams lose water to groundwater by outflow through the streambed and thus regarded as a losing stream. For this condition to exist, the stream must be above the groundwater table, and water moves from the channel into the surrounding ground
- Streams gaining and losing in different stream reaches. The condition is more common considering the natural spatial variability of stream geomorphology and alluvial channel aquifer sediment deposition processes.

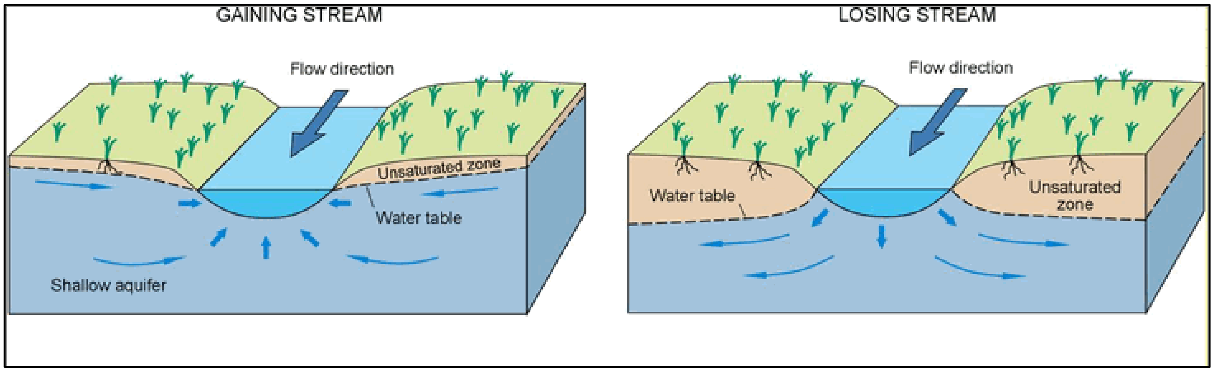

Figure 2.2: A schematic representation of GW-SW interactions occurring through the river/stream bed (taken from Winter et al. 1998)

Groundwater abstraction from aquifers that interacts with river water can have great influence on the quality and quantities of water exchanged with the river system. During the abstraction from boreholes drilled into an alluvial channel aquifer that is hydraulically connected to a gaining stream, groundwater flux into the stream can be significantly reduced (Gomo, 2011). Groundwater over abstraction however, can potentially result in the hydraulic gradient reversal hence the groundwater flow direction. Furthermore, under losing stream conditions, groundwater abstraction from the adjacent alluvial channel aquifer increases stream loses (Gomo, 2011). The effects of groundwater abstraction will not be investigated in this thesis because the study site comprises of ideal natural groundwater flow conditions. It is the core objective of the study to investigate GW-SW interactions that occur under natural groundwater flow conditions.

2.4.2 Approaches for GW-SW interaction investigations and other SW-GW studies

Madlala (2015) highlighted that the importance of interaction of surface and groundwater and their role as an important part in integrated water resources management (IWRM) and allocation has recently, gained much attention worldwide. Understanding the dynamics of the surface and groundwater interaction has proven to be a necessity for assessment, characterization and quantification of how the two components impact one another for the sustainable water use and management in catchments with different physiographical conditions (Madlala, 2015). The knowledge required to successfully carrying out the assessment, characterization and quantification of surface and groundwater interaction is therefore vital for carefully selecting a proper method that is defined largely by the physiographical conditions of the catchment. This section further highlights the range of available procedures and techniques used in surface and groundwater interaction studies and finally, the chapter highlights the selected methods and describes them in further detail.

Brodie, et al., (2007) highlighted various types of techniques into 12 categories based on the type of methodologies used to study the surface and groundwater interactions. These techniques are classified into: 1) seepage measurements, 2) field observations, 3) ecological indicators, 4) hydrogeological mapping, 5) geophysics and remote sensing, 6) hydrographic analysis, 7) hydrometric analysis, 8) hyrdochemical and environmental tracer analysis, 9) artificial tracers, 10) temperature studies, 11) water budgets and 12) hydrogeological modelling. With times changing and technology evolving, it became a norm to use multiple techniques on surface-groundwater interaction studies to better the research methods and resulted in improved knowledge on hydrologic and hydrogeologic processes that drive these interactions.

Madlala (2015) further stated that method selection was mainly based on the scale of catchment area which includes the physiographical characteristics, applicability of selected method as well as research objectives. Many of the surface-groundwater interaction studies however, focus on mobility of water between the two components of hydrologic cycle. Studies such as exchange fluxes between surface-groundwater have been well documented globally (Madala, 2015). Various techniques of estimating the rates and directions of exchange have been established and also been replicated worldwide, indicating the varying water resources implications of these interactions in varying physiographical environments (Banks, et al., 2011; Cey, et al., 1998; Ellis, et al., 2001; Kalbus, et al., 2006; Welderufael & Woyessa, 2010; Yang, et al., 2014).

In other similar studies however, various techniques were employed to fulfil their different research objectives as well. For instance, Yang (2018) used some of the above mentioned techniques to fulfil the PhD research looking at the quantitative assessment of groundwater and surface water interactions in the Hailiutu River Basin, Erdos Plateau, China. Yang (2018) presents a systematic approach for investigating the interactions between groundwater and surface water, which consists of a multi-disciplinary approach, was adopted to quantify interactions between groundwater and surface water in the Hailiutu River catchment. The methods include a hydraulic approach, a hydrochemistry and isotope approach, a temperature approach, and a modelling approach. These methods were applied at various spatial and temporal scales from field surveys for chemical and isotopic profile along a tributary to the main river; historical and recent in-situ measurements, and numerical modelling at sub- and catchment scales. A number of conclusions can be drawn from this study:

- The cause-effect analysis identified that precipitation and air temperature had minor effects on flow regime changes, major flow regime shifts were caused by constructions of reservoirs and dikes for surface water diversion, groundwater extraction, and the land use changes.

- The interactions of groundwater and surface water was intensively investigated by means of multiple field measurements for an investigation period of one year in the Bulang sub-catchment, which indicates that groundwater recharge and discharges dominate the hydrological process. The systematic measurements of groundwater levels and temperature all indicate groundwater discharges to the river all year round. About 74.8% of the total river discharge was composed of groundwater discharge even during a heavy rainfall event. A novel estimation of groundwater seepage along the river reach was conducted with combined river discharge measurements and EC profile measurements under natural condition and constant injection. Results show high spatial variability of groundwater seepages along the river.
- The main characteristics of groundwater and surface water interactions in the Hailiutu River catchment is that groundwater constitutes major part of river discharges. Hydrograph separation with daily river discharges from 1957 to 2012 indicates that groundwater discharge accounts for nearly 86% of the total river discharges. Groundwater abstraction has double effects: it increases net groundwater recharge by reducing ET rates, and decreases groundwater discharge to the river by capturing natural groundwater discharge to the river. The interactions between groundwater and surface water as well as the consequences of human impacts should be taken into account when implementing sustainable water resources management in the Hailiutu catchment.
- The findings from the thesis have important implications for water conservation and ecosystem management in the Hailiutu catchment. The water and ecosystem management priority should be to increase groundwater recharge by reducing evaporation loss. Plant species with less evaporation should be selected to vegetate sand dunes. Crops with lower irrigation demands should be promoted to reduce water abstraction. In the future, the Hailiutu River catchment must manage the groundwater recharge for water resource conservation and the maintenance of healthy vegetation.

Gomo (2011) also used some of the above mentioned techniques such as field observation, hyrdochemical and environmental tracer analysis, hydrogeological mapping, water budget and hydrogeological modelling to fulfil the PhD research primarily aimed at investigating the geohydrological properties of the alluvial channel aquifer and its interaction with the river at a local scale of investigation (<1000m). This research was one of the fewer studies conducted in Southern Africa (Bloemfontein in the Free State Province, South Africa) regarding the surface and groundwater interaction.

Furthermore, another surface-groundwater interaction study was conducted in the upper Berg River catchment to assess their suitability in fractured rock environments and assessed potential to improve our understanding on the groundwater-surface water interactions. This study by Madlala (2015) made use of multiple methods including hydrograph, hydrochemical, and differential stream gauging analyses.

Contrary to many of the researches discussed above, the current study aims to a) investigate the role that geology and soils play on water chemistry in the BRC, b) to identify BRC surface and groundwater chemical trends and c) to identify the geochemical processes controlling surface and groundwater chemistry in BRC. This study therefore employed a combination of techniques (i.e. hyrdochemical and environmental tracer analysis and hydrogeological mapping).

CHAPTER 3: RESEARCH DESIGN AND METHODOLOGY

This study was carried out using three types of research designs namely i) Experimental research design; ii) Field research design and meta-analysis research design. According to Thorpe & Holt (2008) field research is defined as a method of data collection that aims to observe, interact and understand people while they are in a natural environment. Field research design allows the researcher to directly collect data. In relation to this study, this research design was employed by means of the researcher collecting primary data in the BRC in 2016 where the water samples were further taken to the Stellenbosch University (ICP-MS and XRF Laboratory) for analysis. Furthermore, an experimental design is a type of research design where the researcher is able to manipulate one or more independent variables and measure their effect on one or more dependent variables. This further enables the researcher to create a set of procedures to test hypothesis. In this research, this method was employed when analysing the water samples for the major cations and anions in the laboratory using Perkin Elmer ICP-OES Optima 5300 DVas well as ThermoFischer Scientific Gallery plus discreet analyser. Arc-GIS and Geosoft were further employed to model the data.

The following methodologies were followed in chronological order to obtain data that will satisfy the set objective:

3.1 Literature Review and Desktop Study

The primary data were obtained from published scientific journals and books, governmental institutions such as Department of Water Affairs and Forestry (Currently known as Department of Water and Sanitation) and the Western Cape Government, Municipalities, Berg River Catchment Management and Berg River Monitoring Programmes. The data were analysed and incorporated into the literature to explain the geology, hydrology and geohydrology of the area and the interaction between surface and groundwater.

3.2 Data from the National Water Monitoring Database

The surface and groundwater data from 2003 to 2013 were obtained from the National Water Monitoring Database owned by the Department of Water and Sanitation. The data can be accessed on the web address below:

http://www.dwa.gov.za/iwqs/wms/data/000key.asp.

3.3 Field work and sample collection

Fieldwork and sampling will be categorized as follows:

- Hydrogeological surveys
- Surface water sampling

3.3.1 Hydrogeological Surveys

The hydrogeological survey for the research consists of small-scale maps of about 1:1000000 to 1:500000. The survey made use of a (Global Positioning System) GPS as well as Arc-GIS32. The GPS was employed to record the location of the surface sample points and the Arc-GIS32 for mapping out the locality of sampled points.

3.3.2 Surface water sampling

The surface water samples were collected in 2016 dry season. The samples were collected from the head waters (Berg River Dam) to the mouth of the river (Laaiplek) by means of grab sample technique. The samples were collected from 23 different locations in the river extent using plastic bottles of 125ml. Each bottle was labelled by a unique identity (numbers i.e. S1, S2 etc).

To ensure accuracy and avoid cross contamination of the samples, the bucket used to collect water sample was first rinsed with deionized water and secondly rinsed with the water from the river before taking the actual sample. When both the bucket and the bottles were rinsed with deionized water, they were further rinsed again with sample water prior to final sample collection and bottling. This procedure was performed at each sample location to avoid contamination of samples.

Moreover, the coordinates of each sample location were recorded using GPS shown in Figure 3.1 below. Physical parameters (TDS, Salinity, pH, EC and Temperature) were immediately analyzed in-situ using M99720 Combo Water Meter in order to get the original nature of sample. The water meter was also rinsed with deionized water prior to taking physical parameter readings from sample water. Thereafter, the samples were stored in cooler box whereby the chemical parameters were analyzed in 24hrs-72hrs at the Stellenbosch University (ICP-MS and XRF Laboratory) for the analysis of chemical parameters (Nitrates, Calcium, Magnesium, Sodium, Potassium, Chloride, Sulphates and Bicarbonates).

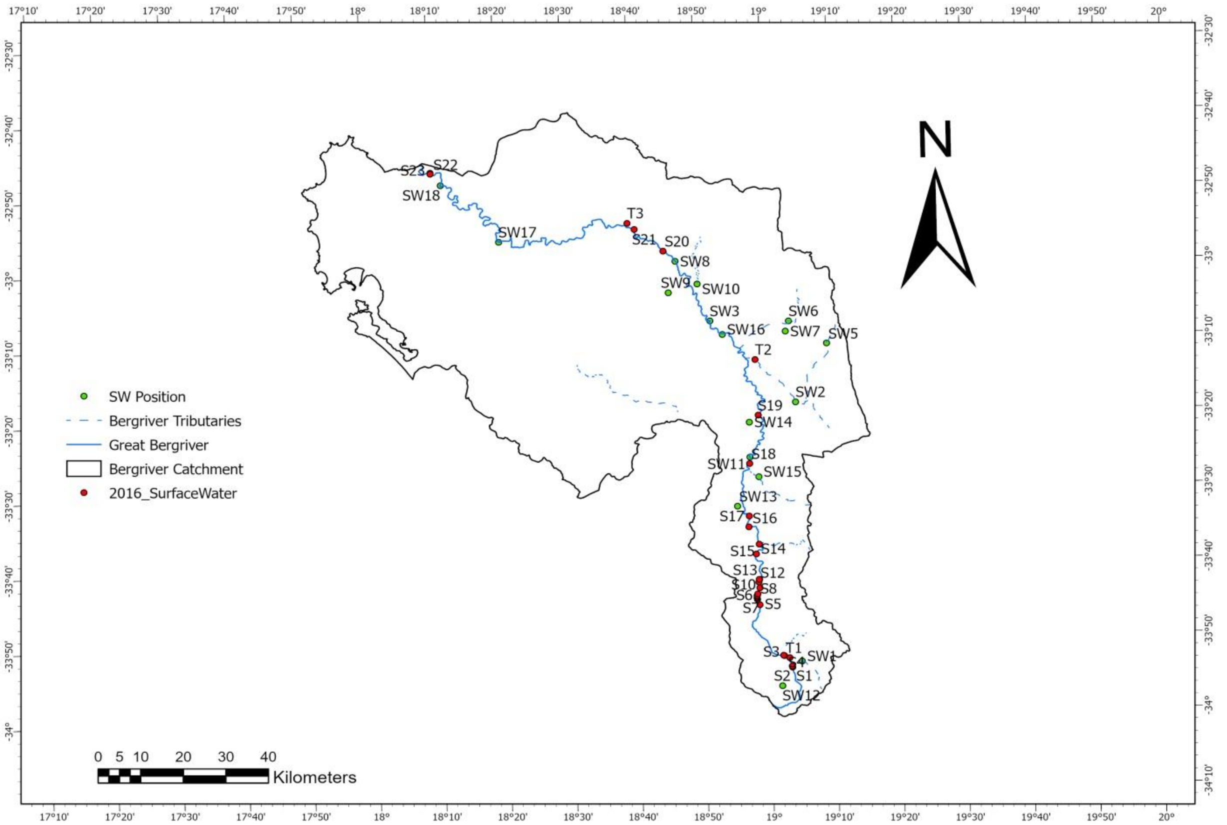

Figure 3.1: DWS Surface Data and 2016 Data sampled by the student

Figure 3.2: Surface sample collection and taking in-situ parameters

3.3.3 2003-2013 Surface and Groundwater hydrochemical data

The surface and groundwater hydrochemical data was obtained from the National Groundwater Archive which is owned by the Department of Water and Sanitation.

3.4 Analysis method for Cat-ions (Ca, Mg and Na+K) using Perkin Elmer ICP-OES Optima 5300 DV

This method describes multi-elemental determinations by ICP-OES using a simultaneous optical system with axial and radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples were nebulized and the resulting aerosol was transported to the plasma torch. Element-specific emission spectra were produced by radio-frequency inductively coupled plasma. The spectra were dispersed by an echelle polychromator, and the intensities of the emission lines were monitored by segmented-array charge- coupled detectors. Simultaneous background correction was performed for each element. The position selected for the background-intensity measurement, on either or both sides of the analytical line, was determined by the complexity of the spectrum adjacent to the analyte line.

3.5 Analysis method for an-ions (Cl, SO_4 and HCO_3) using ThermoFischer Scientific Gallery plus discreet analyser

The Gallery Plus Discrete Analyser is designed to selectively analyse chloride, nitrate and sulphate in water samples based on photometric principles where colour-forming complexing reagents were added to a sample to produce a unique coloured solution for each analyte to be determined. Each unique colour was measured at a specific wavelength where colour intensity (absorbance) was directly proportional to the concentration of the analyte.

3.6 Surface water hydrochemical analysis

The samples collected in 2016 were analysed using Waters 717 autosampler, conductivity detector and Waters2410 pump, controlled with Waters Empower software. An IC Pak A column was used with a Lithium Borate/Gluconate eluent, conductivity 240µS consisting of: 20ml Lithium Borate Gluconate concentrate (34g Boric acid, 23.5ml d-Gluconic acid, 8.6g Lithium hydroxide monohydrate, 250ml Glycerin, filled up to 1litre with

Milli-Q water), 10ml n-Butanol, 120ml Acetonitrile filled up to 1litre with Milli-Q water. 5µl sample was injected for analysis at a flow rate of 1.2ml/min.

3.7 Mapping and Modelling

3.7.1 GW Chart

GW-Chart is a software program used for creating specialized graphs in groundwater studies. The program is able to create several types of graphs such as piper diagrams and hydrographs which were created for this study to provide more understanding of the samples results. To create the piper diagrams, raw data from laboratory which is usually expressed in milligram per litre “mg/l” units were organized into the excel spread-sheet then added onto the GW Chart to create piper plots.

3.7.2 ArcView32a

ArcView comprise one of several ArcGIS software that is used for mapping. This software was used in this study for creation of maps that were used to indicate direction of water flow, sampling points (location), correlation, trends as well as vulnerable areas which are more prone to contamination. The maps were created using excel spread sheet and base maps by means of shapefiles which were obtained from the Department of Rural Development. The excel spread sheet contains correct sampling location (XY coordinates), sample identity and sample contents (chemical parameters) with concentration. The base maps consist of the following layers: rivers, provincial layers, towns and catchment layers.

3.7.3 Oasis Montaj (Geosoft)

Oasis Montaj software was used to grid the Nitrates concentrations in both surface and groundwater data to establish the trends and correlations. The color intensity and scale were used to denote the concentration magnitude of analytes understudied.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents results of the hydrogeological investigations of groundwater and surface water interactions in the Berg River Catchment in Western Cape Province. Both groundwater and surface water were studied in the catchment. Results are presented in graphs, tables as well as maps modelled with Arc-GIS and Geosoft Oasis Montaj. Data was collected in the dry season September 2016. Detailed historical water quality data from 2003 to 2013 were also obtained from the Department of Water and Sanitation. The obtained levels are compared to SANS: 241:2015 and WHO (2011) standards and possible risks inherent are discussed, giving special attention to human health and ecological aspects (aquatic fauna). The in-situ water quality parameters were also measured during sampling and they are temperature, PH, dissolved oxygen and electrical conductivity, refer to **Appendix B.**

4.2 Groundwater Hydrochemical Facies

Hydrochemical facies were used to further analyze the groundwater data in BH1-BH20 respectively. Hydrochemical facies are diagrammatic analysis that are drawn from piper plots that denote the diagnostic chemical aspect of water solutions occurring in hydrologic systems, both surface and groundwater. The facies reflect the response of chemical processes operating within the lithologic framework as well as the pattern of flow of the water. There are 6 hydrochemical facies namely: i) NaCl, ii) CaCl, iii) $CaHCO_3$, iv) Mixed-CaMgCl, v) Mixed-$CaNaHCO_3$ and $NaHCO_3$. In this study, the hydrochemical facies helped in identifying the quality of water by grouping the chemical data into 5 hydrochemical facies namely: i) NaCl, ii) CaCl, iii) $CaHCO_3$, iv) Mixed-CaMgCl and v) Mixed-$CaNaHCO_3$. The table below illustrates the various hydrochemical facies of the groundwater data from BH1-BH20.

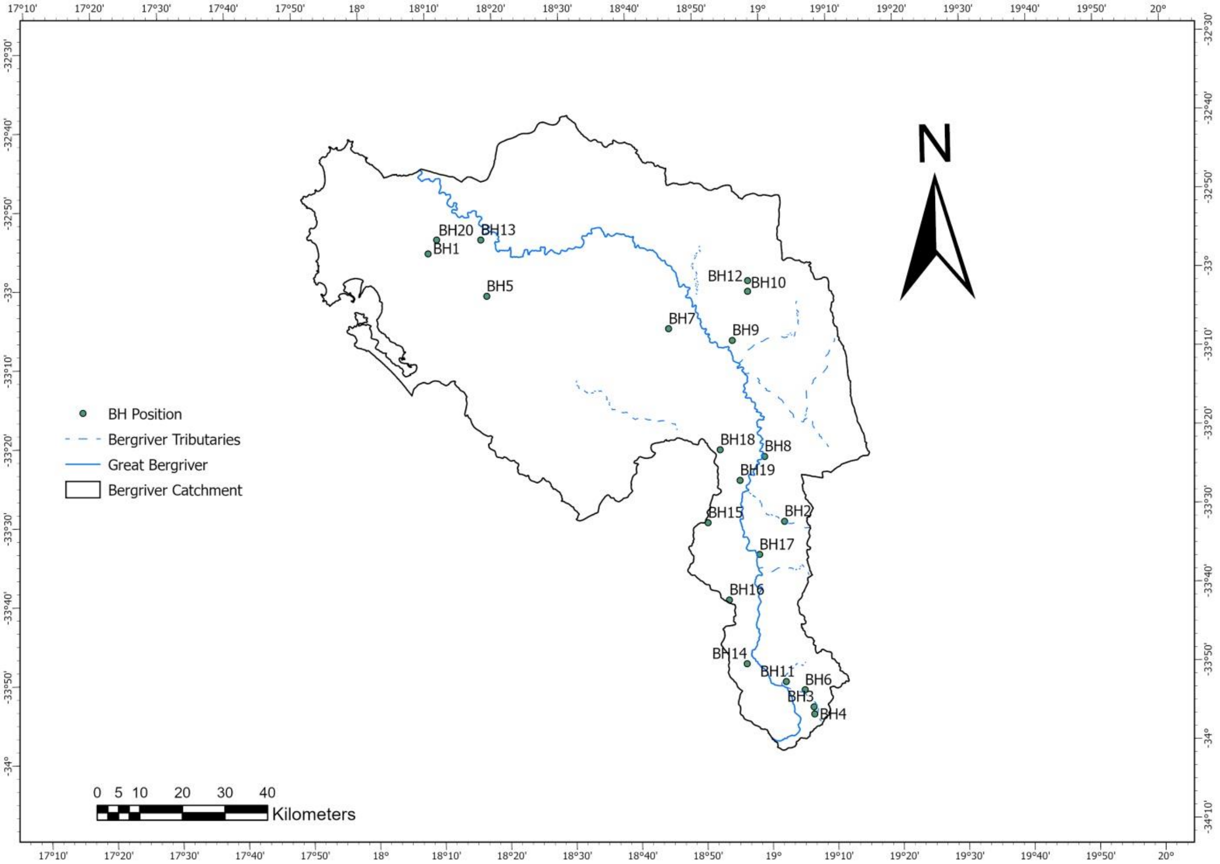

Figure 4.1: Borehole locality Map

Table 4.1: Summary of GW Hydrochemical Facies

Borehole Identity	**Hydrochemical Facies**
1. BH1	NaCl
2. BH2	NaCl ; Mixed CaMgCl
3. BH3	$CaHCO_3$; NaCl; Mixed $CaNaHCO_3$; Mixed CaMgCl
4. BH4	$CaHCO_3$; Mixed $CaNaHCO_3$; NaCl
5. BH5	NaCl
6. BH6	NaCl ; $CaHCO_3$; Mixed $CaNaHCO_3$
7. BH7	NaCl
8. BH8	NaCl
9. BH9	NaCl
10. BH10	NaCl
11. BH11	NaCl ; $CaHCO_3$; CaCl
12. BH12	NaCl ; $CaHCO_3$
13. BH13	NaCl
14. BH14	NaCl

15. BH15	NaCl
16. BH16	NaCl ; Mixed CaMgCl
17. BH17	Mixed CaMgCl ; NaCl
18. BH18	Mixed CaMgCl ; NaCl
19. BH19	NaCl
20. BH20	NaCl

2003-2006 groundwater chemistry data

The previous chapters have emphasized on the variability of the water quality in the stretch of the BRC, as a result the use of trilinear piper diagrams aims to depict the picture of the surface and groundwater quality within the catchment for the period of 11 years between 2003 and 2013. The piper diagram in Figure 4.2 showed that 15 of 20 boreholes had water type of NaCl, while 2 boreholes: BH6 and BH12 indicated the dominancy of $CaHCO_3$ water type. BH6 had further shown consistency with $CaHCO_3$ hydrochemical facies between the years 2003-2005 as shown in Figures 4.2-4. Although BH6 had water type of $CaHCO_3$, the trilinear plots representing the cations in 2003-2004 showed that BH6 did not have dominant cation of those that belong to the carbonate group, but rather had mixed cations. The BH6 dominant anion was HCO_3 and was consistent for 2003-2004. Nonetheless, the BH6 $CaHCO_3$ facie suggests the chemical weathering of carbonate bed rocks such as limestone. The area is however; underlain by geology comprised of pebbly quartz arenite, diamictite, minor conglomerate, mudrock, siltstone and shale. This may be a result of other sources like anthropogenic activities.

On contrary, BH12 showed consistency of NaCl type throughout the years (Figures 4.3-11) except in the year 2003 in Figure 4.2. BH12 showed $CaHCO_3$ facies only in 2003 with very minimal ionic concentrations and changed to NaCl facie from 2004 with varying ionic concentrations of Na and Cl respectively. The Na cation ranged from 88.8mg/L to 142.94mg/L whereas the Cl anion ranged from 165.8mg/L to 235.29mg/L which are compliant with the standards stipulated in Table 1.4. The hydrochemical facies presented by BH12 suggest the dissolution of salt bearing rocks such as phyllite and limestone as well as minerals such as albite. The area is underlain by limestone which justifies the presence of the $CaHCO_3$ facie.

The 2003 dataset showed that BH4 had no dominant water type as it is on the margin of $CaHCO_3$ type and Mixed-$CaNaHCO_3$ type in Figure 4.2. On a larger scale however, BH4 can be seen fluctuating between $CaHCO_3$ type and Mixed-$CaNaHCO_3$ type throughout the years as shown in Figures 4.2-12. The locality of the borehole indicates that the underlying geology constitute quartzitic sandstones as well as limestone, as a result the two BH4 hydrochemical facies suggest the dissolution of limestone as well as silicates containing Na such as albite.

BH2 can be seen on the margin of NaCl and Mixed-CaMgCl facies throughout the years as shown in Figures 4.2-12. The water types of BH2 suggest chemical dissolution of carbonate rock such as limestone and dolomite as well as NaCl bearing rocks such as phyllite and albite. This borehole however, showed above average concentrations of Cl ranging between 231.861mg/L to 406.9mg/L throughout the selected years for this research. With reference to Table 1.4 of drinking water standards, the borehole was not fully compliant in terms of Cl concentrations as some years the Cl is above the permissible quantity.

Furthermore, the trilinear diagrams indicated that BH18 showed consistency with Mixed-CaMgCl water type for most of the years between 2003 and 2010 shown in Figures 4.2-10. However, in 2011 and 2012 the groundwater data for BH18 showed a dominant water type of NaCl. This suggest the weathering of various rock types including carbonate rocks resembling dolomite and limestone although the geology of the area has several minor lithologies such as quartzitic sandstone, subordinate silt and shale and greywacke quartzite. The sudden change in hydrochemical facie to NaCl however, suggests that there might have been human influence.

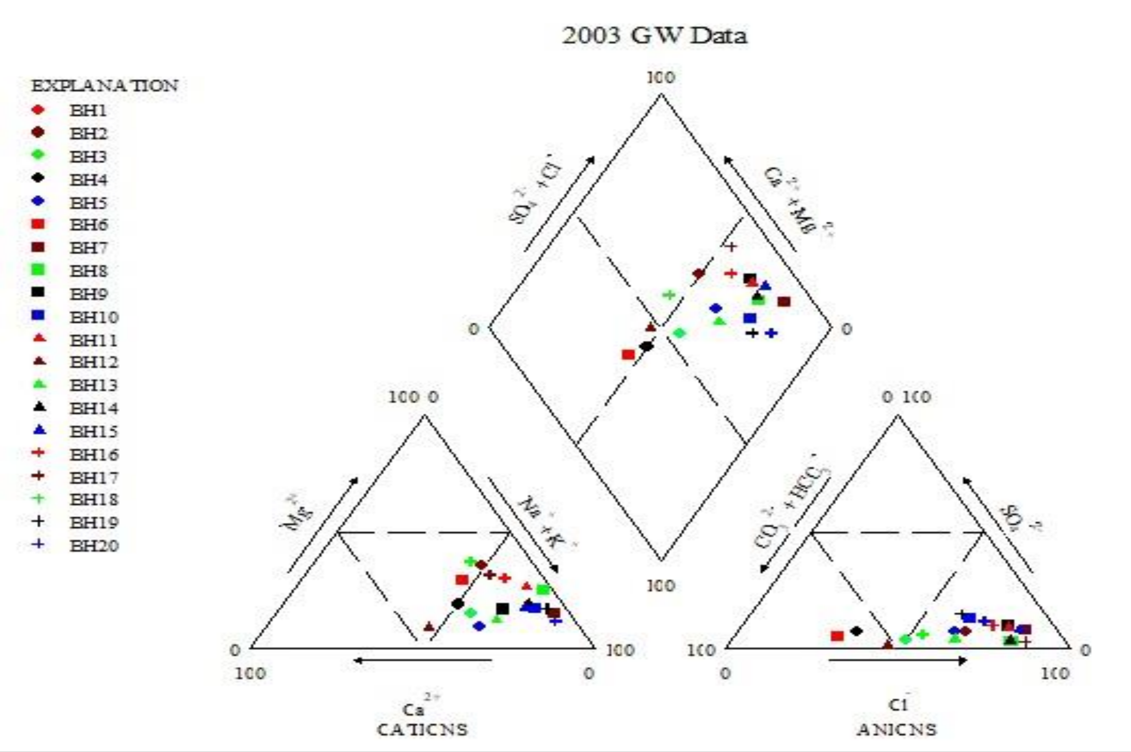

Figure 4.2: 2003 groundwater chemistry data plot

Figure 4.3 showed groundwater data for 2004 which indicated minor similarities with those of 2003 data plot such as the consistency on BH6 with $CaHCO_3$ hydrochemical facie and BH18 with Mixed-CaMgCl hydrochemical facie, even though BH18 also showed some increased Ca, Mg and Cl concentrations. BH4 however has changed from $CaHCO_3$ to Mixed-$CaNaHCO_3$ type. Notably, BH3 has changed from NaCl water type to $CaHCO_3$ type while all other 17 of 20 boreholes showed dominant NaCl type for 2004 dataset. BH3 is situated in the headwaters and therefore is expected to indicate a replica of rainwater or pure water as the geology of the area is mostly sandstones and minor limestones (Clark & Ractliffe, 2007). In addition, there are minor siltstones in the headwaters which may be responsible of the NaCl however, with reference to other boreholes in the same area as BH3, it can be deduced that BH3 has an external factor contributing to its consistent NaCl.

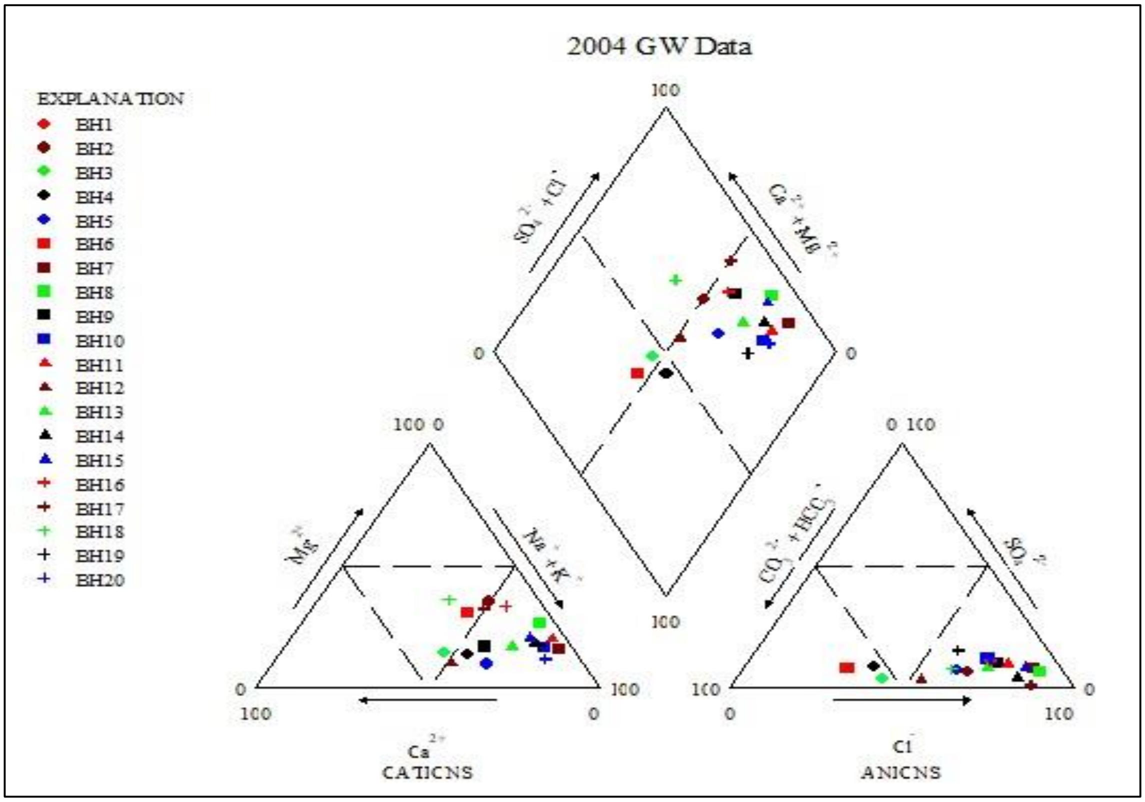

Figure 4.3: 2004 groundwater chemistry data plot

As mentioned above, the NaCl hydrochemical facie suggest disturbances of groundwater quality by activities such as irrigation with saline water which may have enhanced NaCl concentrations as the area is heavily cultivated. Geologically, the headwaters is made up of white coarse-fine grained, thick bedded pebbly quartz arenites, thin bedded feldsphathic and ferruginous sandstone, subordinate shale and siltstone and as a result, salt in groundwater was not expected.

BH2, BH12 and BH17 have plotted in between NaCl and Mixed-CaMgCl facie. BH12 has however changed from $CaHCO_3$ type in 2003. This borehole is situated in the vicinity of G10H quaternary catchment known for the towns of Porterville and Picketburg where the underlying geology comprise phyllitic shale, subordinate dolomite and limestone,. The underlain geological setting thus explains the $CaHCO_3$ type, Mixed-CaMgCl as well as the NaCl type which is however, the dominant water type for these boreholes through the selected years despite 2003.

The groundwater datasets for 2005 and 2006 showed other 16 of 20 boreholes having dominant water type of NaCl. Nonetheless, BH3 showed fluctuations of water types ranging from NaCl in 2003, to $CaHCO_3$ in 2004 to margin of Mixed-CaMgCl and $CaHCO_3$ in 2005 in Figure 4.4 and back to $CaHCO_3$ facie in 2006 in Figure 4.5 below. The fluctuation of water quality in BH3 not only suggest bedrock weathering of sandstone of the TMG but also suggest other factors playing a role such as human interferences which may be responsible for the presence of salinity in groundwater. Although some years BH3 showed NaCl facie, the NaCl concentrations were well within the permissible limit as per the drinking water quality standards. The values of Na ranges between 18.403mg/L to 25.357mg/L while Cl values range between 29.553mg/L to 40.019mg/L. consequently, BH3 have other hydrochemical facies that indicates dominance of karst environment. The values of Ca, Mg and HCO_3 are also well within the permissible limits with Ca ranging from 7.857mg/L to 17.031mg/L, Mg ranging from 2.636mg/L to 5.107mg/L and HCO_3 from 31.1mg/L to 59.59mg/L.

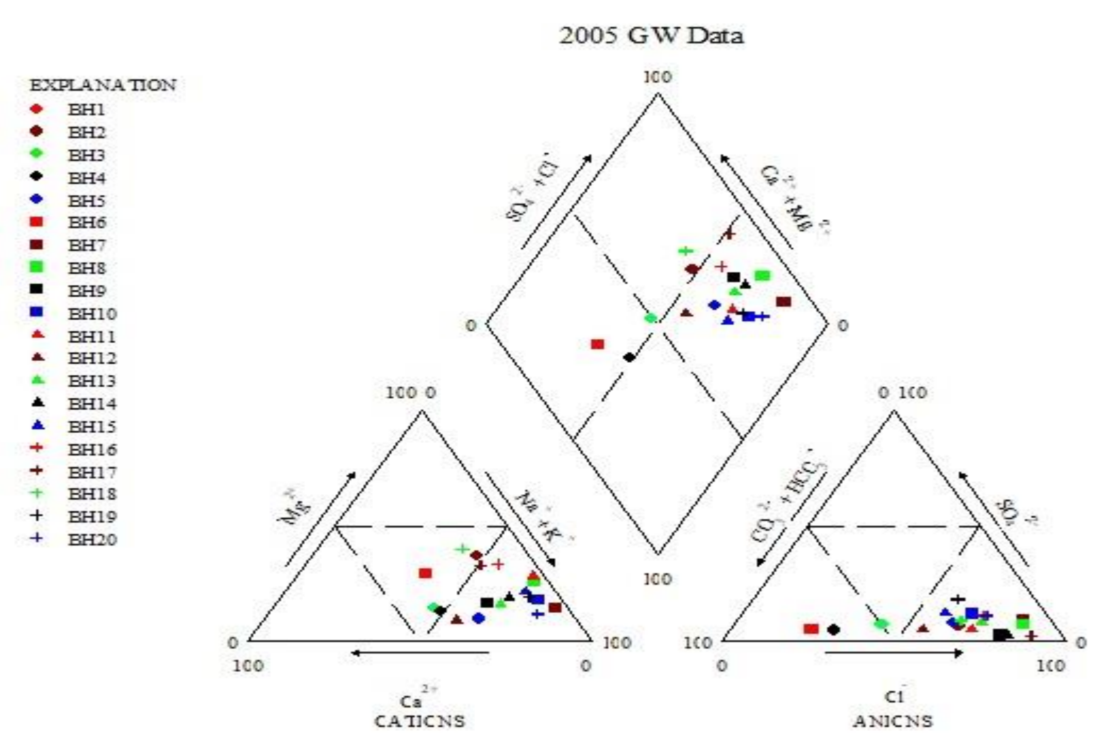

Figure 4.4: 2005 groundwater chemistry data plot

Similar to BH3, BH6 locality is in the headwaters however, the borehole water quality data can be observed fluctuating between $CaHCO_3$ during 2003-2005, Mixed-$CaNaHCO_3$ in 2006 and NaCl from 2007-2013 in Figure 4.6-4.12. The changes suggest a form of external interference, which introduces salinity into groundwater as the geology. Between 2005 and 2006, the piper diagrams have shown BH18 in the same position with Mixed-CaMgCl facie however, with reduced cations and anions concentrations. BH4 have also changed facies from in between $CaHCO_3$ and Mixed-$CaNaHCO_3$ in 2005 to $CaHCO_3$ in 2006 with increased Ca and HCO_3 concentrations.

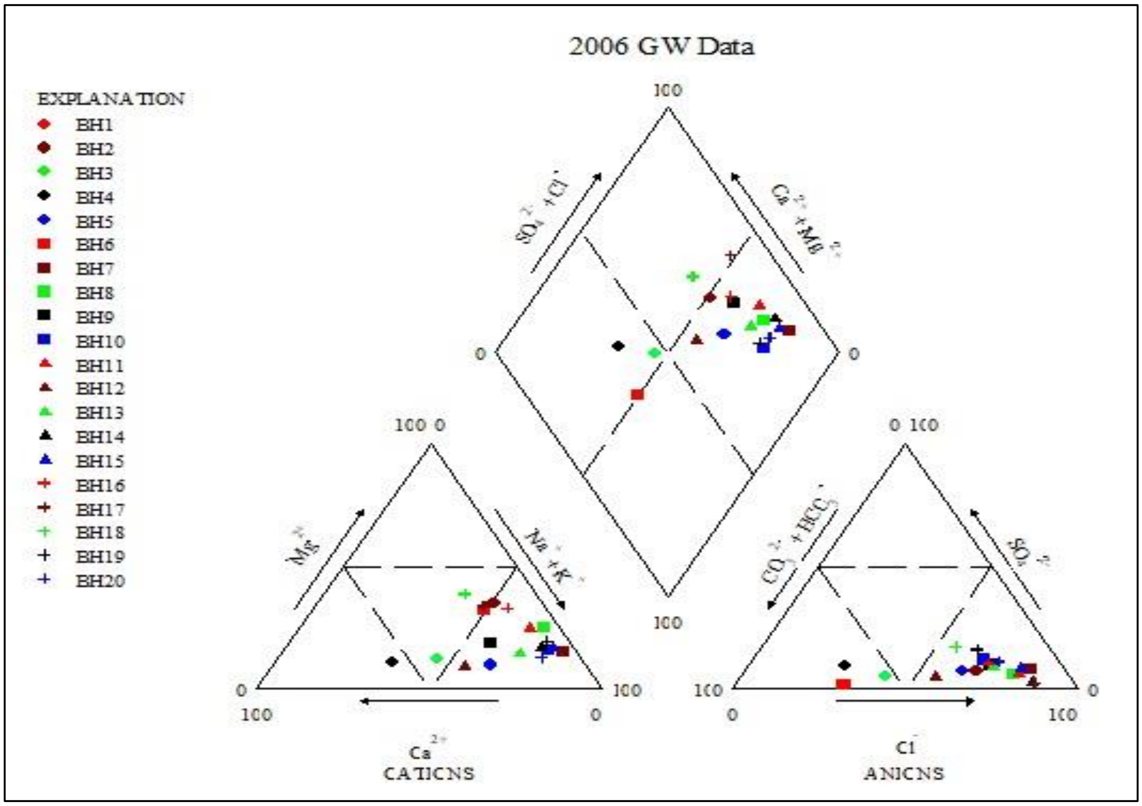

Figure 4.5: 2006 groundwater chemistry data plot

2007-2010 groundwater chemistry data

Figure 4.6 and 4.7 shows the 2007 and 2008 data which indicated slight increase in Ca and HCO_3 concentrations for BH4 as compared to the 2005 and 2006 datasets. The 2008 data however, indicate a slight reduction in HCO_3 concentrations for BH4. Such parameter fluctuation are expected as the underlying geology comprise variety of rocks including white coarse-fine grained, thick bedded pebbly quartz arenites, thin bedded feldsphathic and ferruginous sandstone, subordinate shale and siltstone. Furthermore, the piper diagram still showed BH3 fluctuating between $CaHCO_3$, Mixed-$CaNaHCO_3$, Mixed-CaMgCl and NaCl facies in 2008. Notably, BH6 had changed facies completely from $CaHCO_3$ and Mixed-$CaNaHCO_3$ facies to NaCl facies with increased Na and Cl concentrations in 2007 though the concentrations lessened in 2008. As said earlier in the Chapter, BH6 is situated in the headwater whereby the underlying geology resembles very little possibility of weathering of salt bearing rocks (Clark & Ractliffe, 2007). As a result, the presence of salt may not be the result of the underlying geology but rather other external factors.

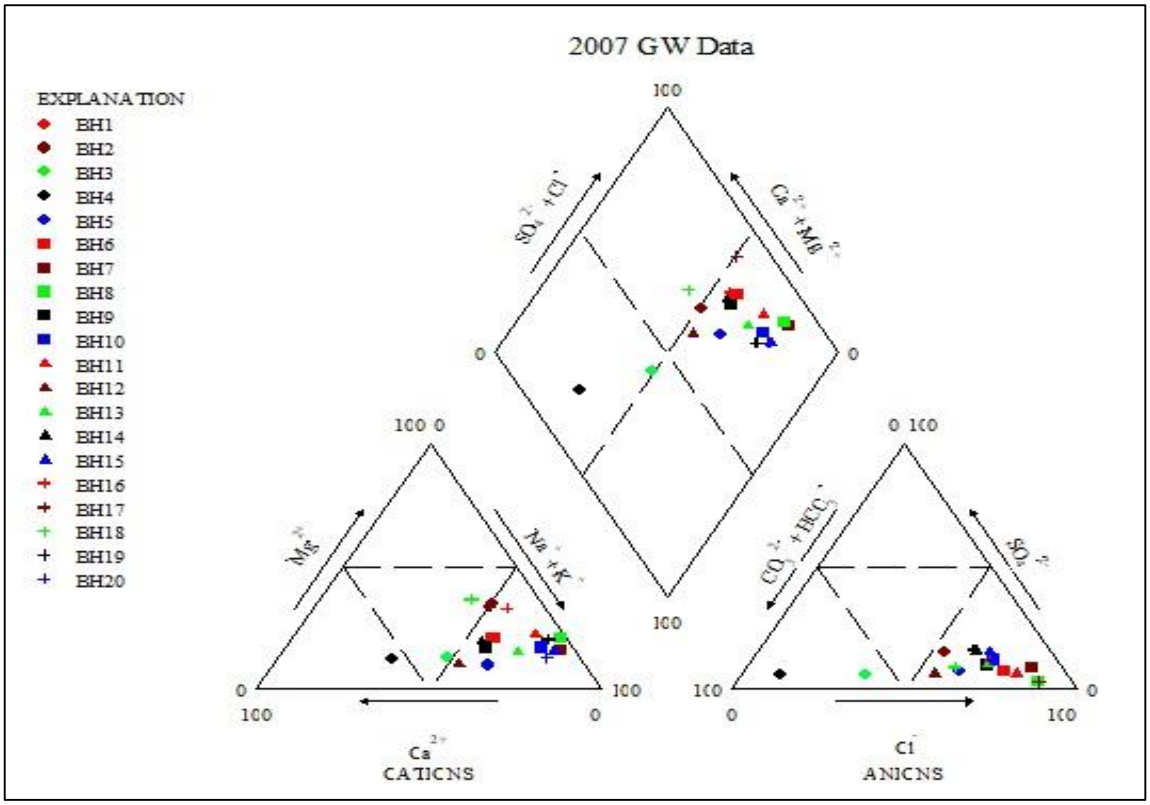

Figure 4.6: 2007 groundwater chemistry data plot

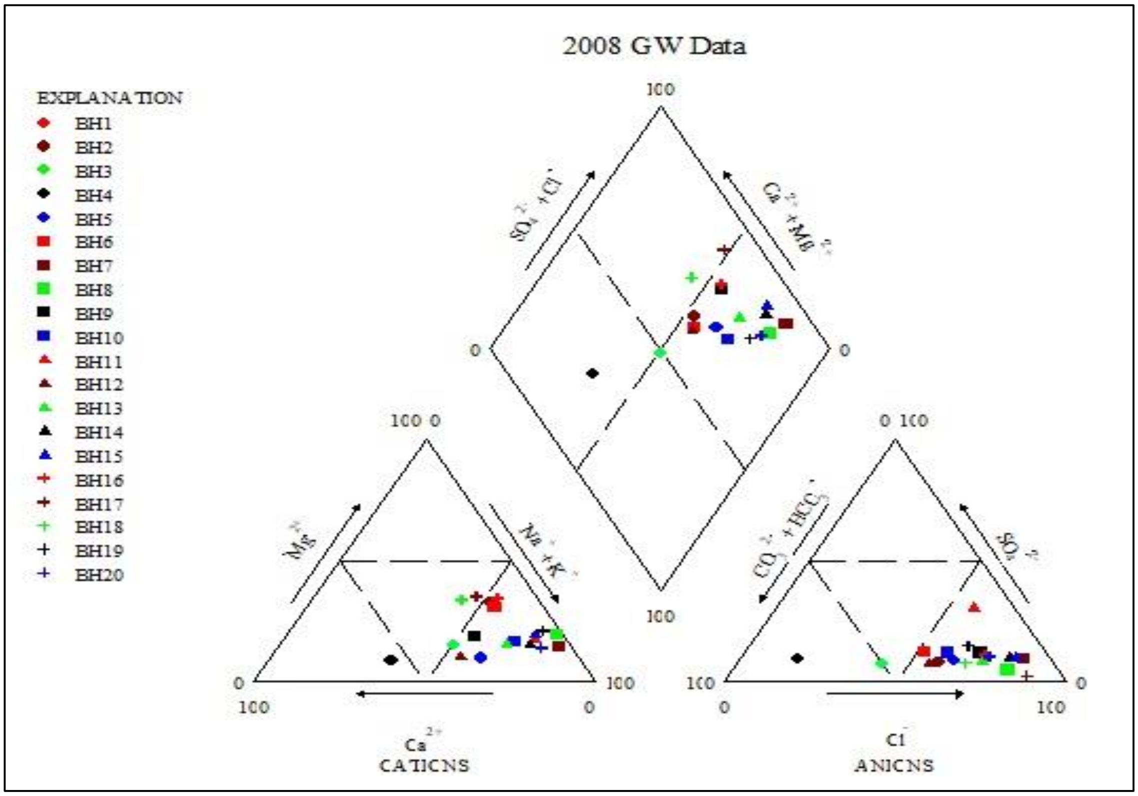

Figure 4.7: 2008 groundwater chemistry data plot

A small change can be observed for groundwater data for 2009 in that BH11 had for the first time since 2003 shown a change in facie from the NaCl type to CaCl water type. Similar to BH2, BH3, BH4 and BH6; BH11 is situated nearer to the head water wherein, according to Clark & Ractliffe (2007), the water quality is not expected to be of saline nature. Traces of Na and Cl elements do not point to the weathering of the underlying geologic material since the underlying geology is of TMG group dominated by sandstone and minor limestone. Furthermore, BH17 also maintained the migration between Mixed-CaMgCl and NaCl water type however; this was projected since the area where BH17 is located is underlain by carbonate rocks such as dolomite and other types of rocks including phyllite shale, quartzite and greywacke. Furthermore, BH3 indicated NaCl hydrochemical facie again since it last shown this facie in 2003. The facies for BH3 had been consistent throughout the years and the sudden change to NaCl once in a while does not indicate geological weathering.

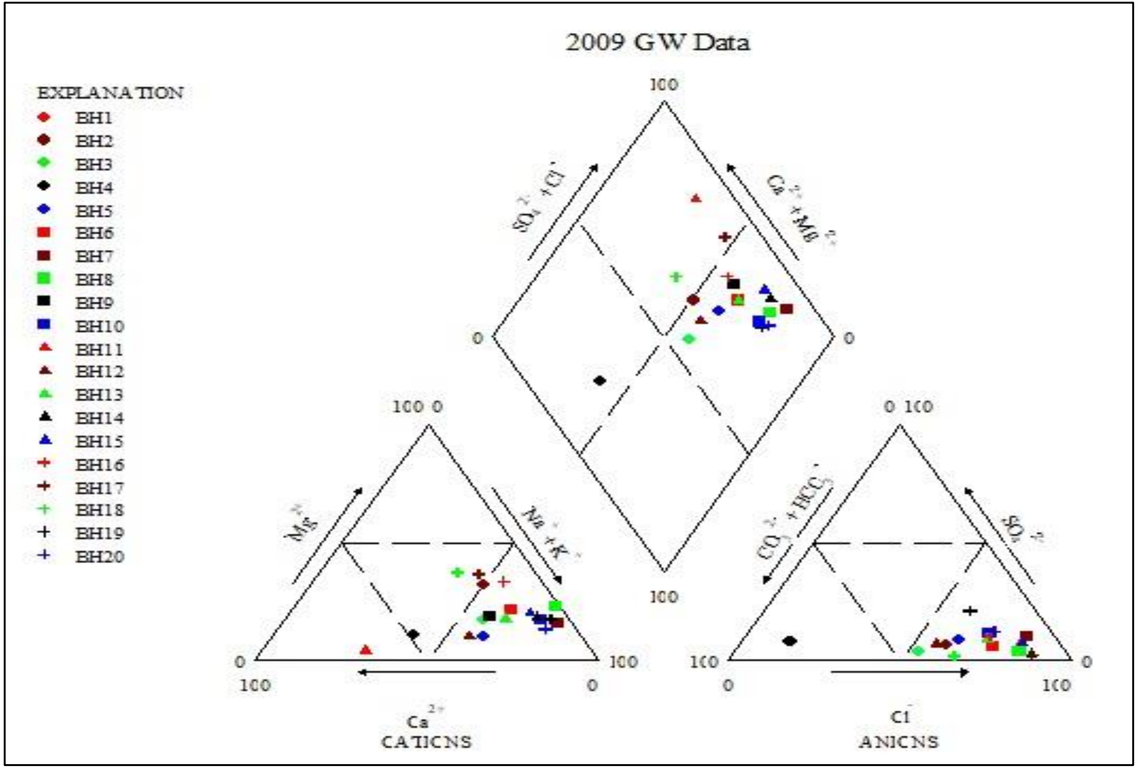

Figure 4.8: 2009 groundwater chemistry data plot

Figure 4.9 represent groundwater facies for 2010 wherein, there was a minor change in BH16. The BH16 water type also changed from NaCl to Mixed-CaMgCl for the first time since 2003 however, the BH16 further changed back to NaCl from 2011-2013. Although the area where the BH16 is situated is underlain by dolostones and minor Malmesbury shale, the groundwater quality has since 2003 maintained the water type of NaCl, as a result the sudden change indicate that there has been interference for the longest of time such that the water type was NaCl.

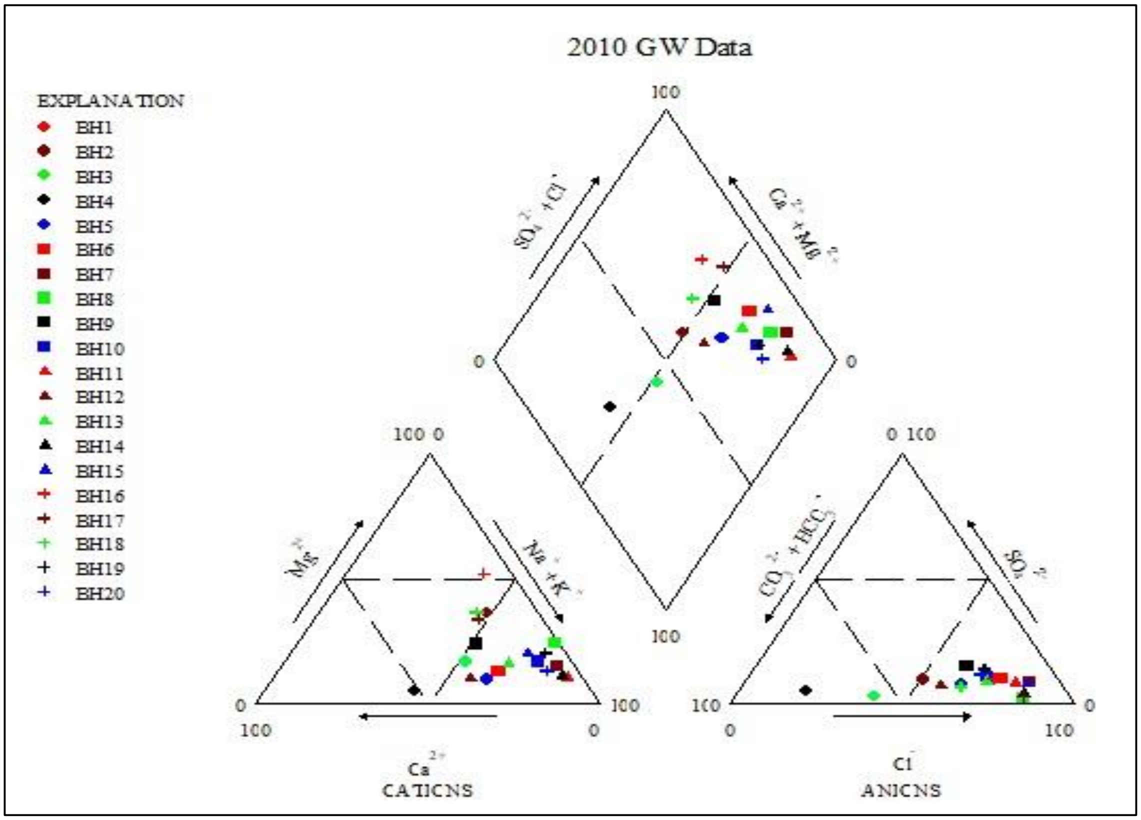

Figure 4.9: 2010 groundwater chemistry data plot

2011-2013 groundwater chemistry data

The trilinear facies for 2011 illustrated a significant change in many borehole data in that almost all the boreholes have NaCl water type. Only BH3 and BH4 are on the margins of NaCl and Mixed-CaMgCl water types. Given the varying geologic setting of the catchment from the headwater to the ocean, it is not expected that all borehole facies would indicate the NaCl facie. The representation in Figure 4.10 indicates an interference of groundwater where there is an induced NaCl. Furthermore, the 2012 data represented in Figure 4.11 showed that some of the boreholes now indicate their normal groundwater facies. For instance, BH2, BH4 and BH18 changed back to their facies. However, BH11 has further shown another different water type of $CaHCO_3$ for the first time since 2003. Figure 4.11 also shows BH3 changes back to NaCl for the 3rd time in the duration of the research after years of fluctuating margins of $CaHCO_3$ and Mixed-$CaNaHCO_3$.

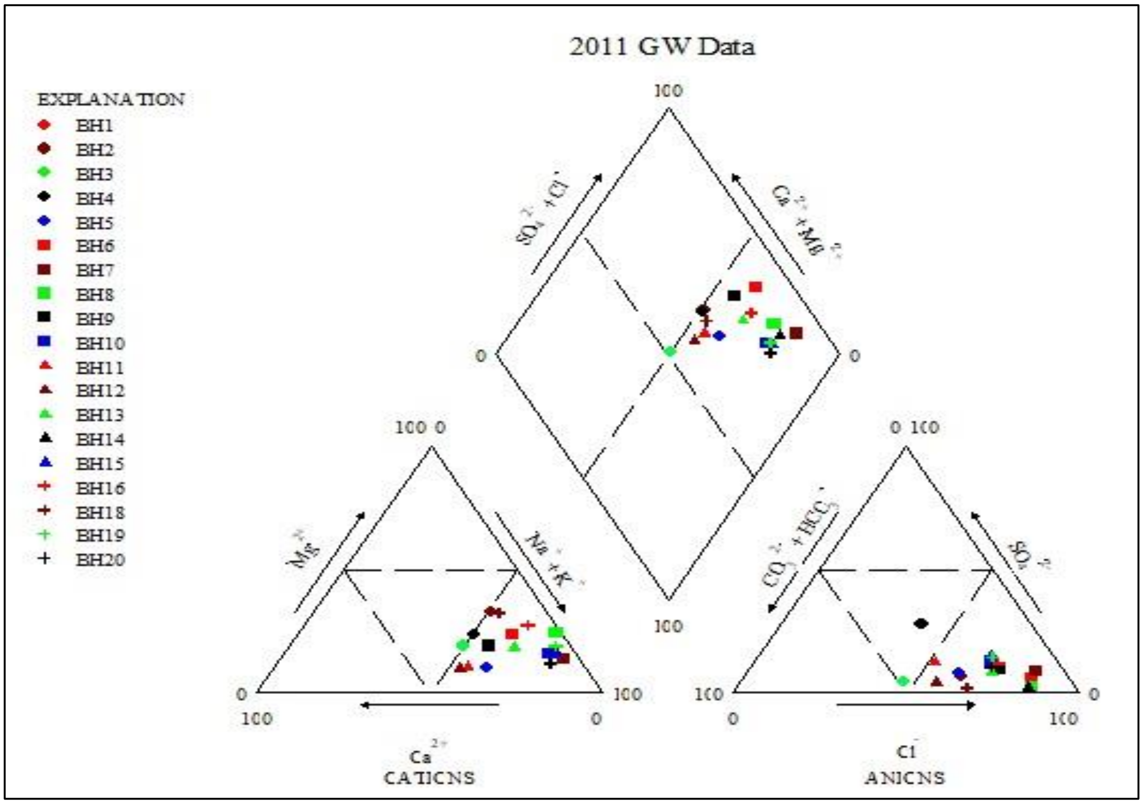

Figure 4.10: 2011 groundwater chemistry data plot

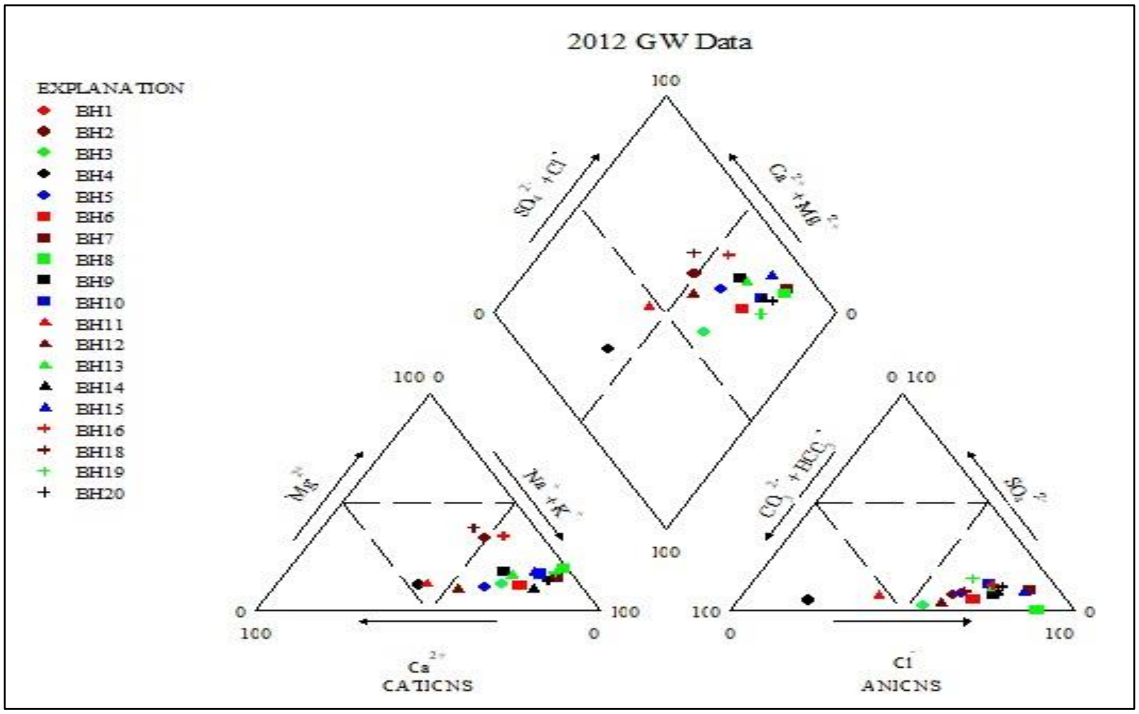

Figure 4.11: 2012 groundwater chemistry data plot

The 2013 data does not show much variability as 17 of 20 boreholes shows dominance of NaCl water type. BH11 however, remain with the $CaHCO_3$ type with increased concentrations in Calcium and Bicarbonate as compared to in 2012. BH18 also still remain in Mixed-CaMgCl water type although with increased concentration of Ca and Mg and decreased concentrations of Cl. BH4 on the hand further shows changes from $CaHCO_3$ type to Mixed-$CaNaHCO_3$ type with increased Sodium and Bicarbonate.

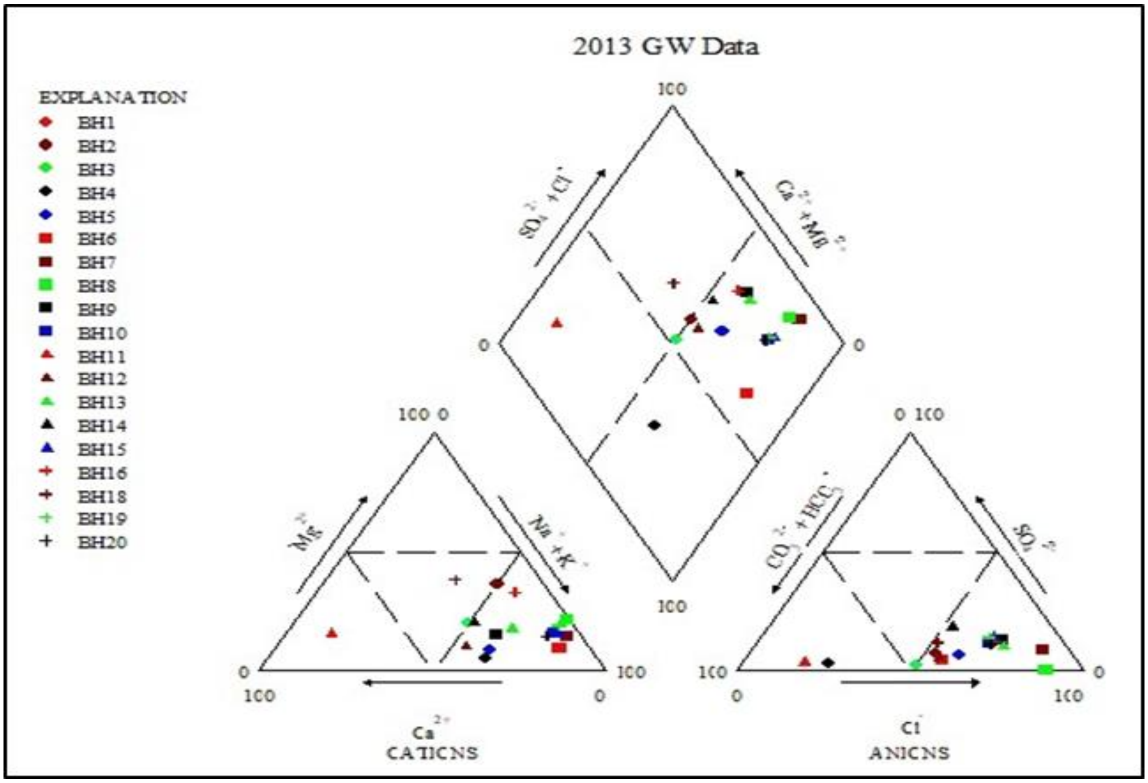

Figure 4..12: 2013 groundwater chemistry data plot

4.3 Surface water hydrochemical facies

Hydrochemical facies were used to further analyze the surface water data in SW1-SW18 respectively. Hydrochemical facies are diagrammatic analysis that are drawn from piper plots that denote the diagnostic chemical aspect of water solutions occurring in hydrologic systems, both surface and groundwater. The facies reflect the response of chemical processes operating within the lithologic framework as well as the pattern of flow of the water. In this study, the hydrochemical facies helped in identifying the quality of water by grouping the chemical data into 3 hydrochemical facies namely: i) NaCl, ii) Mixed-CaMgCl and iii) $CaHCO_3$. The table below illustrates the various hydrochemical facies of the surface water data from SW1-SW18.

Table 4. 2: *Summary of Surface water samples hydrochemical facies*

Sampling Point ID	**Hydrochemical Facie**
1. SW1	NaCl ; Mixed-CaMgCl
2. SW2	NaCl
3. SW3	NaCl ; Mixed-CaMgCl
4. SW4	NaCl ; Mixed-CaMgCl
5. SW5	NaCl ; Mixed-CaMgCl ; $CaHCO_3$
6. SW6	NaCl ; Mixed-CaMgCl
7. SW7	NaCl ; Mixed-CaMgCl ; $CaHCO_3$
8. SW8	NaCl
9. SW9	NaCl
10. SW10	NaCl
11. SW11	NaCl
12. SW12	NaCl ; Mixed-CaMgCl ; $CaHCO_3$
13. SW13	NaCl
14. SW14	NaCl ; Mixed-CaMgCl
15. SW15	NaCl
16. SW16	NaCl
17. SW17	NaCl
18. SW18	NaCl

2003-2006 surface water chemistry data

The surface water quality data also indicated a variation in the water types existing within the catchment. While majority of the water samples have been consistent with the NaCl water types, a few of them indicated variation and inconsistencies. Sample points such as SW4, SW5 and SW6 are amongst those which have shown a variation of hydrochemical facies throughout the 11 years of the data collected. Between 2003 and 2006 alone, SW5 have presented three different facies amongst which are $CaHCO_3$ in 2003; NaCl in 2004 and 2005 and in 2006 this sample point had no dominant water types as it were between the $CaHCO_3$ and Mixed-CaMgCl water types. Similarly, SW6 showed no dominant water type in 2003 and 2006, instead the sample data presented the two water types; NaCl and Mixed-CaMgCl. However, in 2004 the SW6 indicated a dominant water type of NaCl and Mixed-CaMgCl in 2005. SW5 and SW6 are in the same vicinity, therefore the hydrochemical facies thus suggest the chemical weathering of geological setting such as phyllite shale (with dominant chlorite and silicates), greywacke and limestone which the area of sample points is comprised of.

Furthermore, SW4 had also shown an interchange of water types between 2003 and 2006. In 2003, SW4 had no dominant water type instead it were in between the NaCl and Mixed-CaMgCl water types whereas in 2004 its dominant water type was NaCl and in 2005 it were Mixed-CaMgCl and further carried on to interchange between the two abovementioned water types. SW4 is situated in the area of Paarl wherein the geology is made up of Porphyritic, medium-fine grained granite and granodiorite with subordinate syenite, gabbro, and diorite and quartz porphyry. As a result, the hydrochemical facies suggest amongst other external factors, the weathering of granodiorite family of rocks comprised of augite which is a rock forming pyroxene mineral with formula $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$.

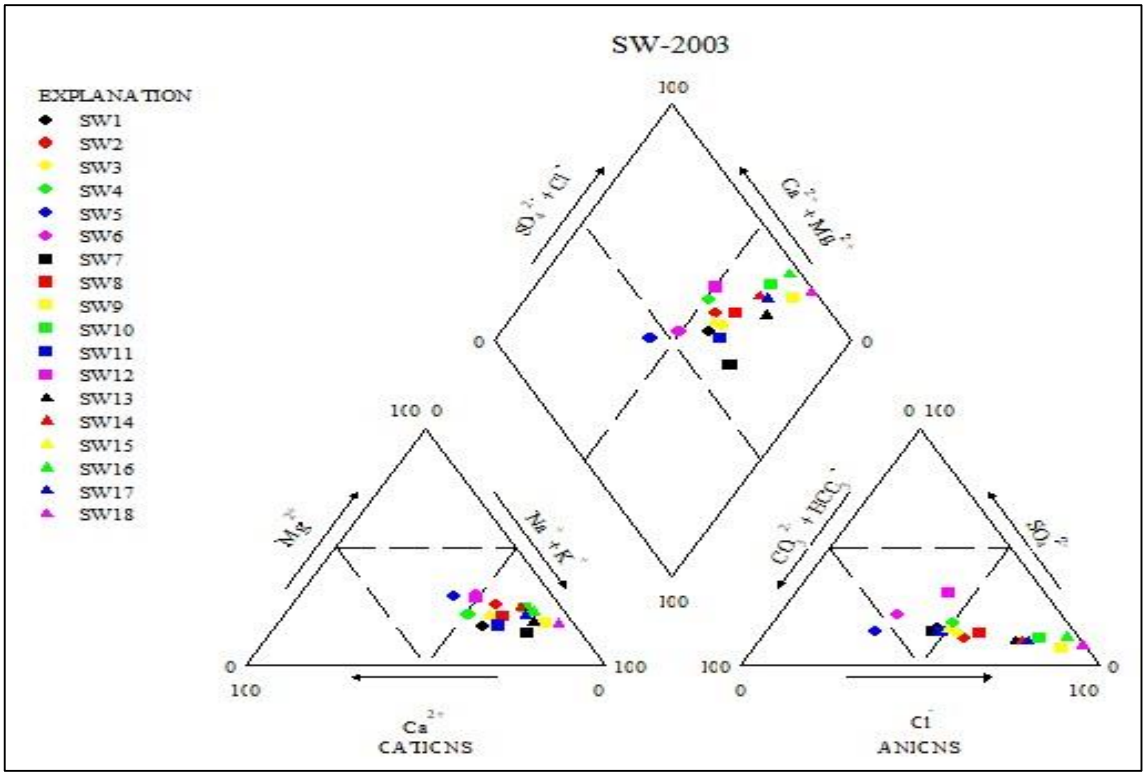

Figure 4.13: 2003 surface water chemistry data plot

Amongst other surface water sample points which had shown occasional changes in water types are SW1, SW3 and SW12. SW1 had however not shown much variation, in most years this sample point had shown the NaCl water type however; in 2005 it had a mixed-CaMgCl as its dominant water type. Similarly, SW3 had few cases where the water type was changed from NaCl to mostly Mixed-CaMgCl type. SW12 on the other hand indicated somewhat similar patterns as those of SW4 and SW6, as it also fluctuated between the NaCl and Mixed-CaMgCl water types. Both SW1 and SW12 are situated in the headwater with the geological make-up of quartzite, conglomerate and slate and the geological make up cannot be seen as the reason for the presence of NaCl in particular but rather human activities.

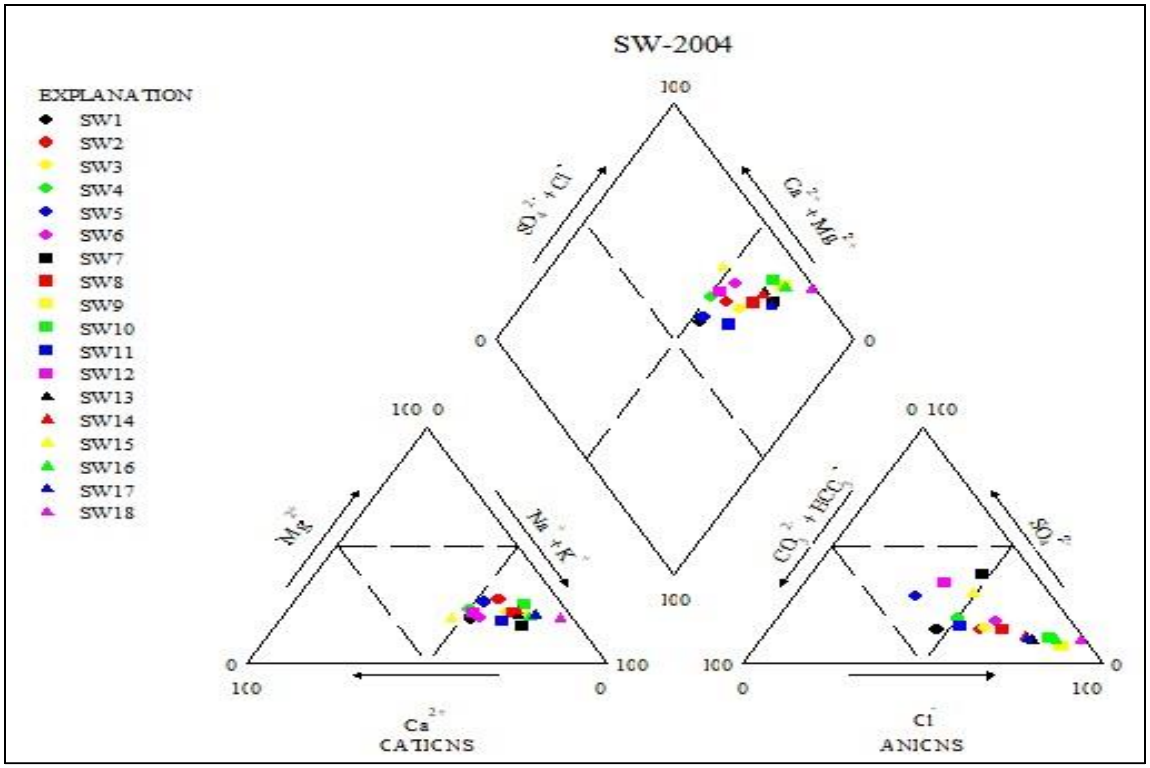

Figure 4.14: 2004 surface water chemistry data plot

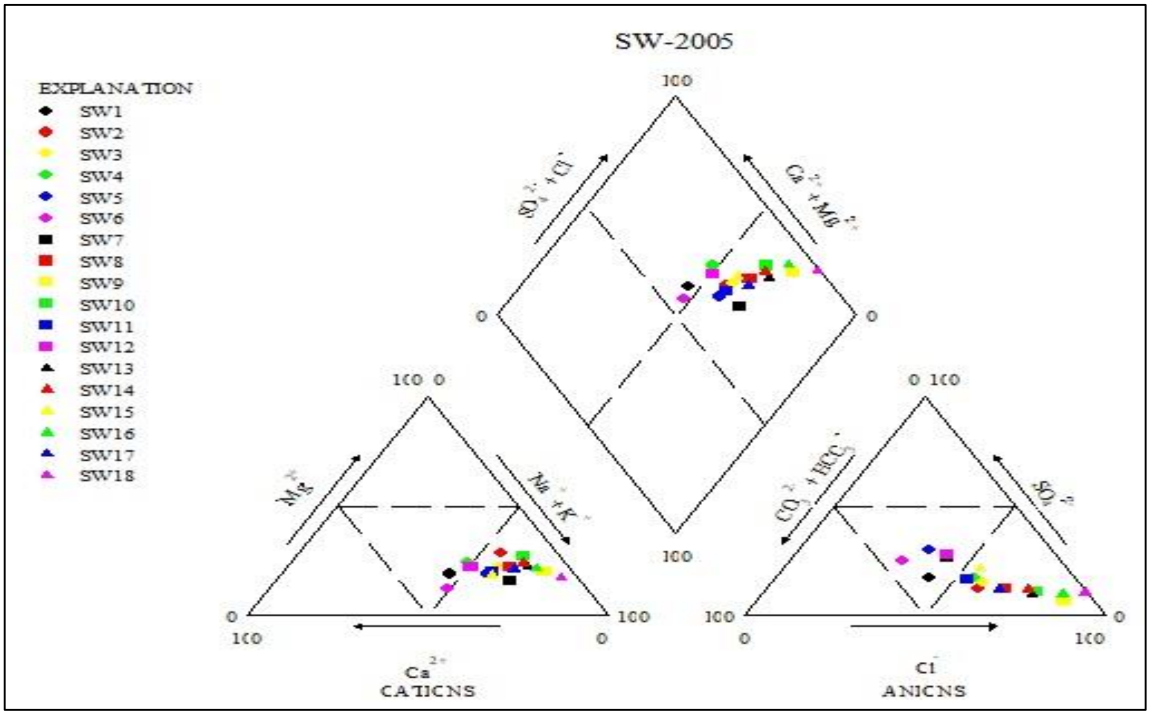

Figure 4.15: 2005 surface water chemistry data plot

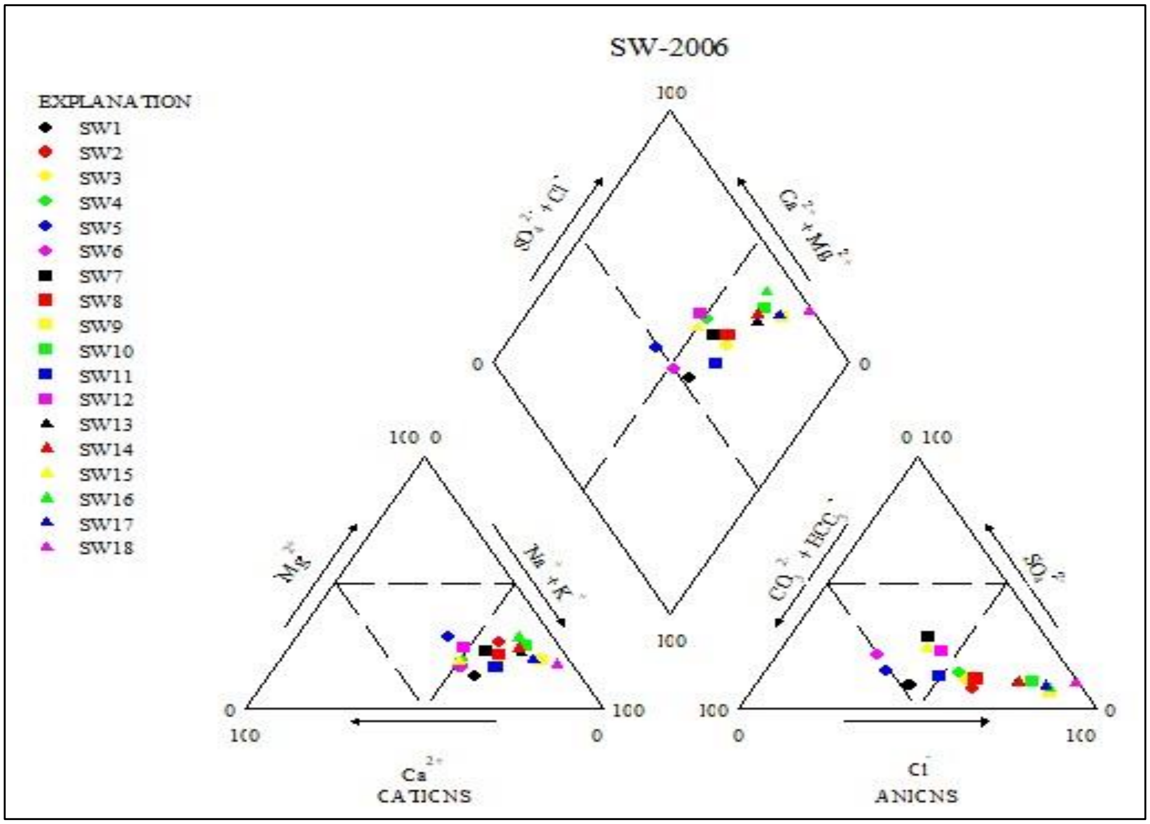

Figure 4.16: 2006 surface water chemistry data plot

2007-2010 surface water chemistry data

The 2007 surface water sample points had shown that all the sample points had a dominant NaCl water type. In 2008 however, SW12 showed $CaHCO_3$ as a dominant water type. This had however occurred once since 2003-2010, meaning it could have been an incidental discharge of materials dominant with such parameters as it has since been changing between the NaCl and Mixed-CaMgCl water types. In addition, SW5 had also been in between the NaCl and Mixed-CaMgCl water types in 2008 and was further in between three water types in 2009 and 2010 namely: $CaHCO_3$, Mixed-CaMgCl and NaCl. SW7 had been consistent with the NaCl water type since 2003 however; the diagrams indicate a slight migration towards $CaHCO_3$ water type in 2009 but changed to Mixed-CaMgCl type in 2010. SW7 is located in the same area as SW5 and SW6 therefore chemical weathering of geological setting such as phyllite shale (with dominant chlorite and silicates), greywacke and limestone may be taking place along with the SW-GW interaction.

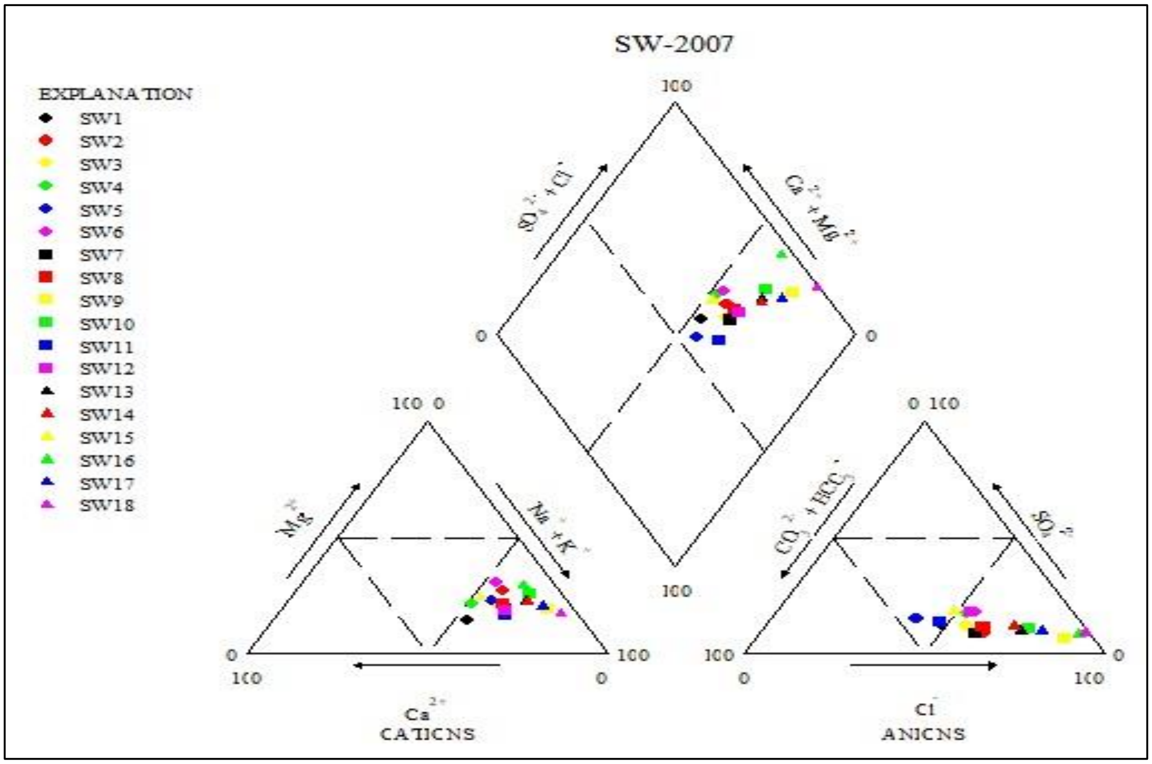

Figure 4.17: 2007 surface water chemistry data plot

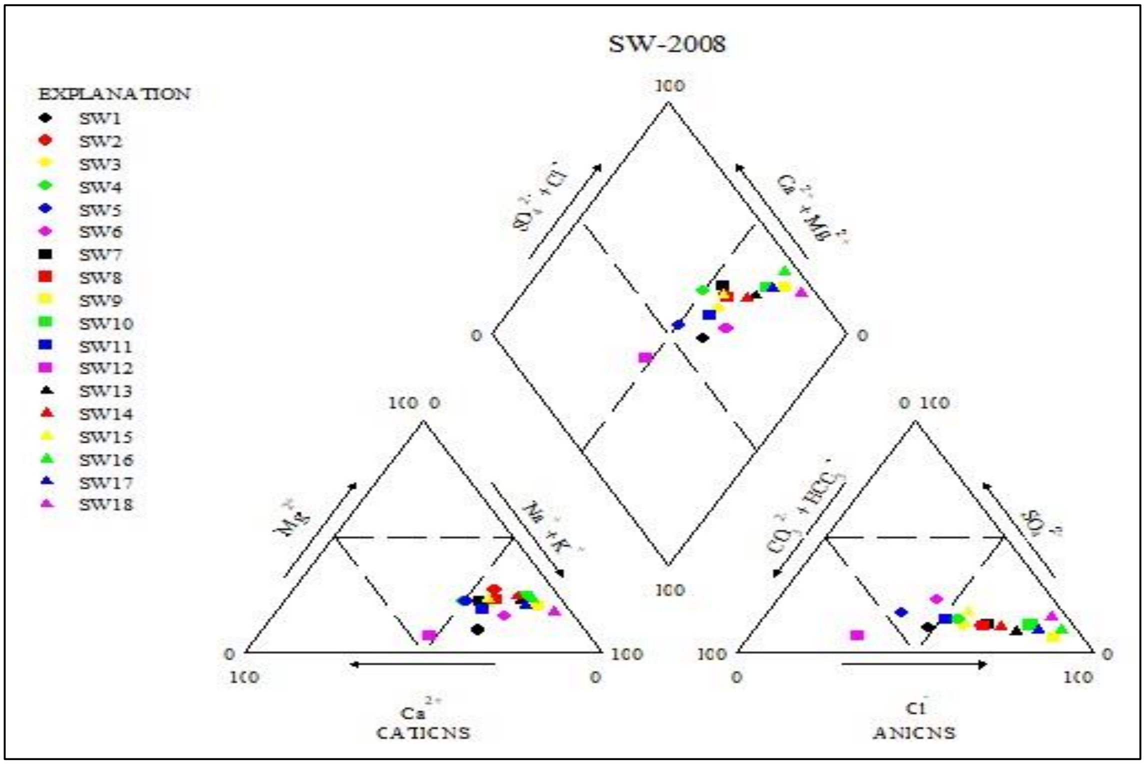

Figure 4.18: 2008 surface water chemistry data plot

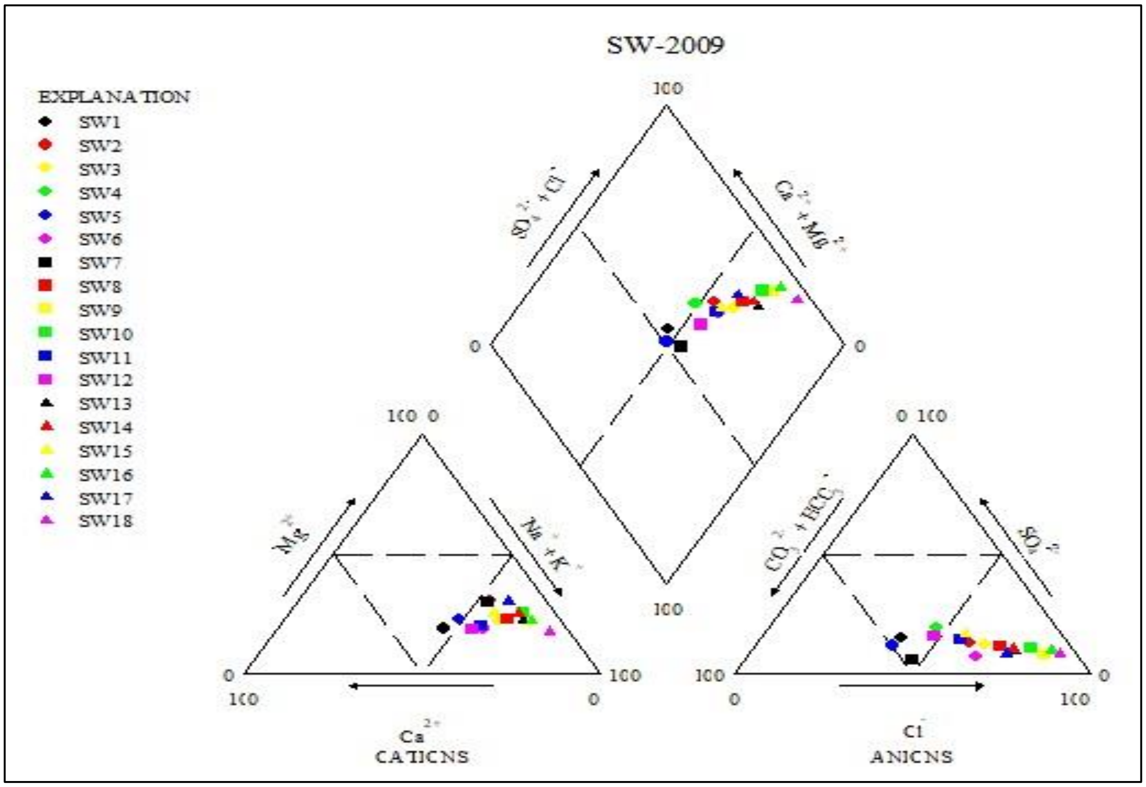

Figure 4.19: 2009 surface water chemistry data plot

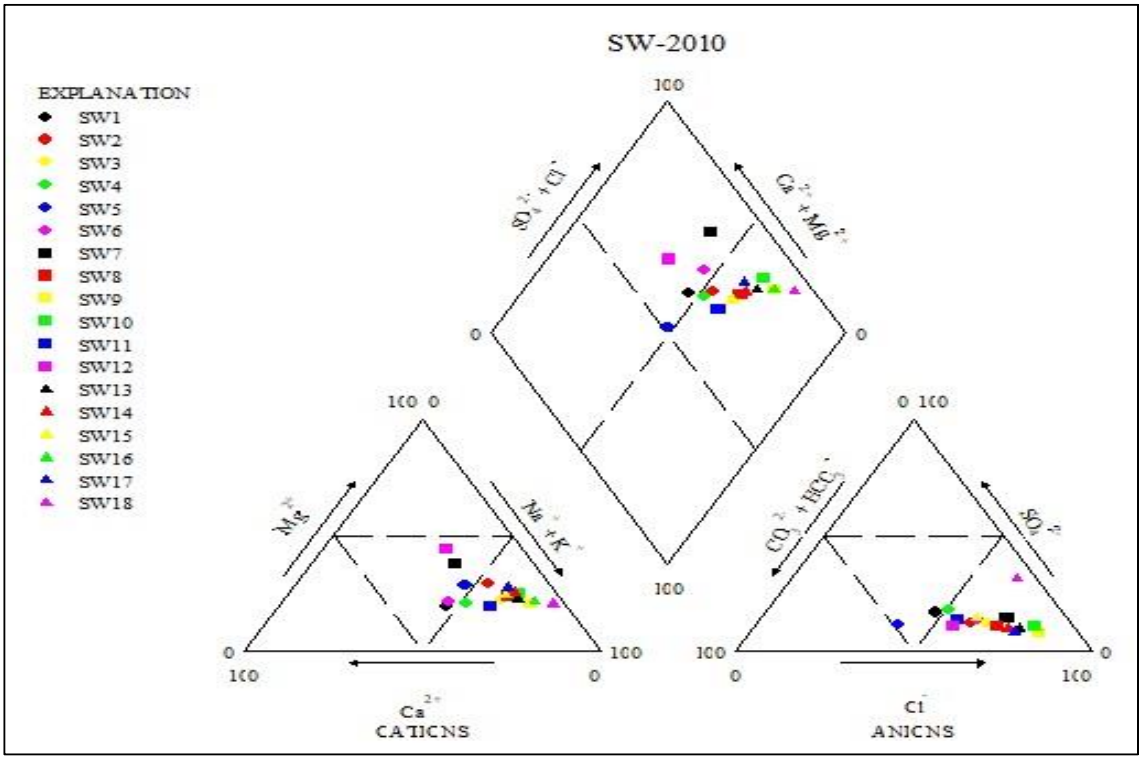

Figure 4.20: 2010 surface water chemistry data plot

2011-2013 surface water chemistry data

The 2011-2013 surface water quality did not present much difference from the previous years. With that said, SW4, SW6 and SW12 were still changing between the NaCl and Mixed-CaMgCl water types while SW5 also fluctuated between $CaHCO_3$, Mixed-CaMgCl and NaCl. A slight change can be observed from SW14 in 2012 when it presented the Mixed-CaMgCl water type for the first time since 2003; this may have been an accidental discharge of materials containing Calcium and Magnesium.

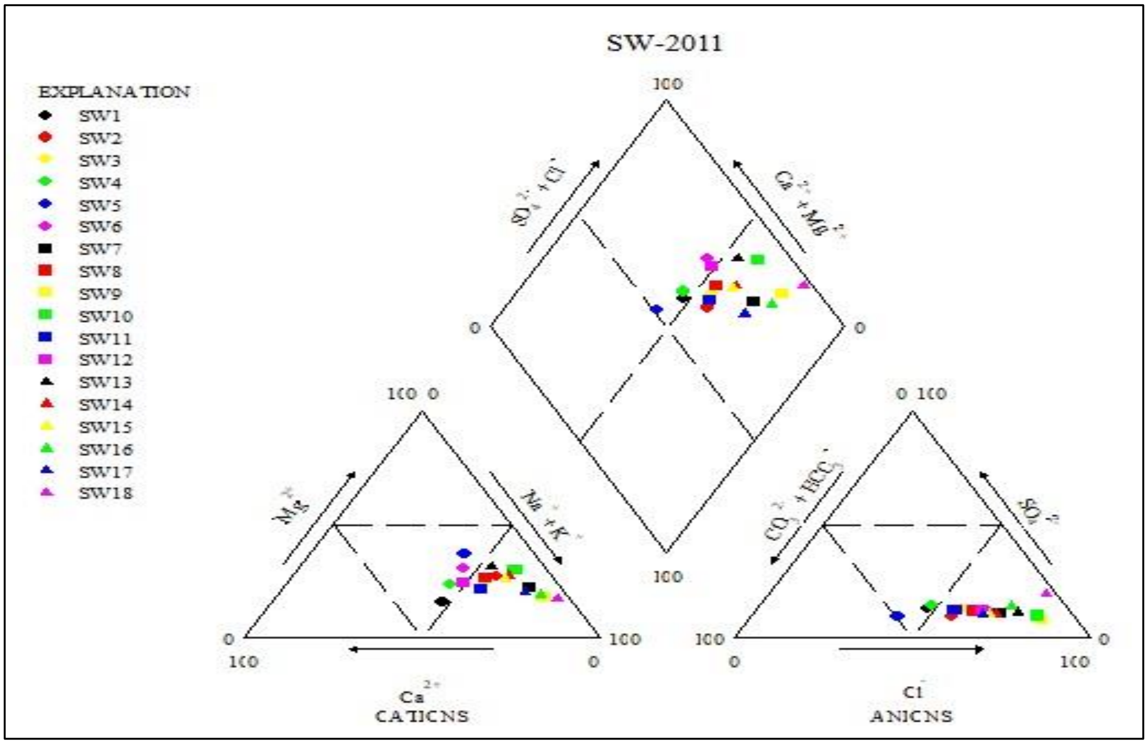

Figure 4.21: 2011 surface water chemistry data plot

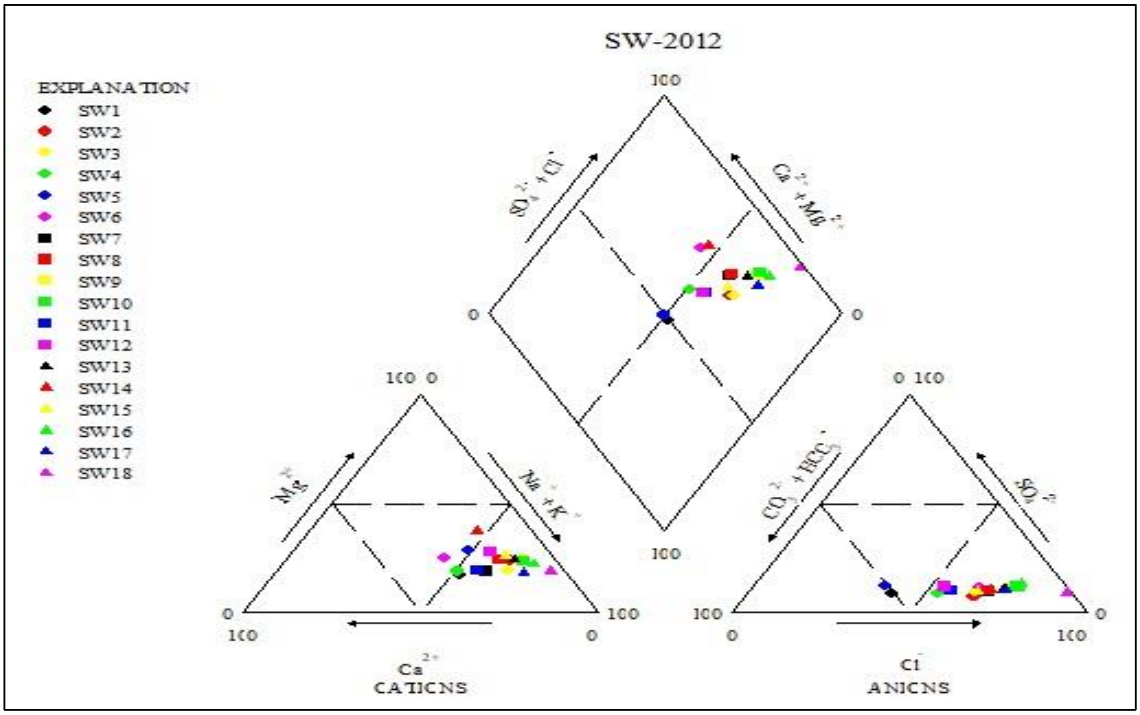

Figure 4.22: 2012 surface water chemistry data plot

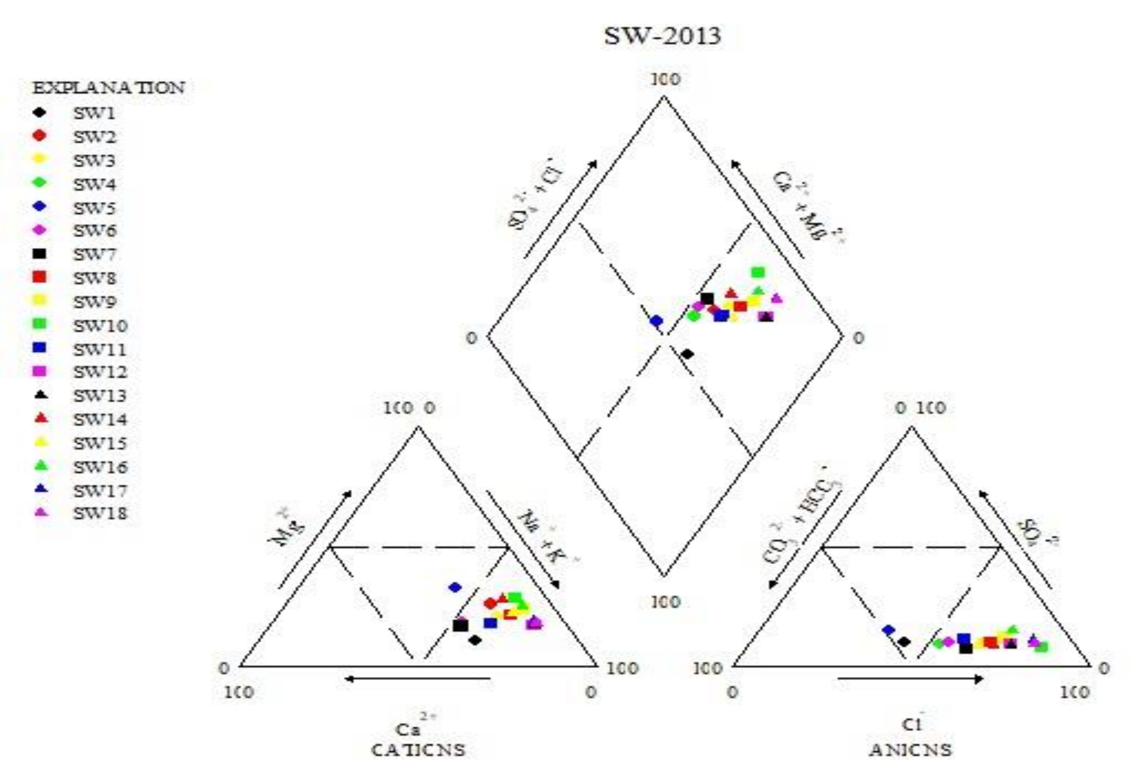

Figure 4.23: 2013 surface water chemistry data plot

4.4 Groundwater NO3-+NO2- variations in the BRC

Several studies have highlighted that nitrates have for some years become an environmental issue in certain areas of the BRC such as the Mbekweni informal settlements just outside Paarl, as well as others which have ailing sewage infrastructure. As a result of dynamic hydrological system, groundwater may be affected by excess nitrates from surface water. Below are the results of nitrate trends obtained from the BH1-BH20 in the BRC.

2003-2006 groundwater nitrates data

The 2003-2006 data shown in Figure 4.24-4.27 indicated that BH1, BH9, BH18 and BH20 had the highest nitrate concentrations with BH20 being the highest with the values of 16.657mg/L in 2003 and 11.086mg/L in 2006 was being its lowest record in the abovementioned four years. BH1 and BH9 showed fluctuations of high nitrate concentrations ranging between 8mg/L and 11.368mg/L. Furthermore, BH18 also showed fluctuations of low-high nitrate concentrations with 2003 being its lowest with the value of 0.354mg/L and 2004 being its highest with the value of 12.205mg/L. The BRC is heavily cultivated from the headwaters down to the river mouth; as a result, it is very unclear as to why certain sample points such as SW1, SW20, SW9 and SW18 (discussed later in the chapter) record higher nitrates than others. However another reason could be due to irrigation using the river water which may have been affected by malfunctioning sewage plants and other human induced activities.

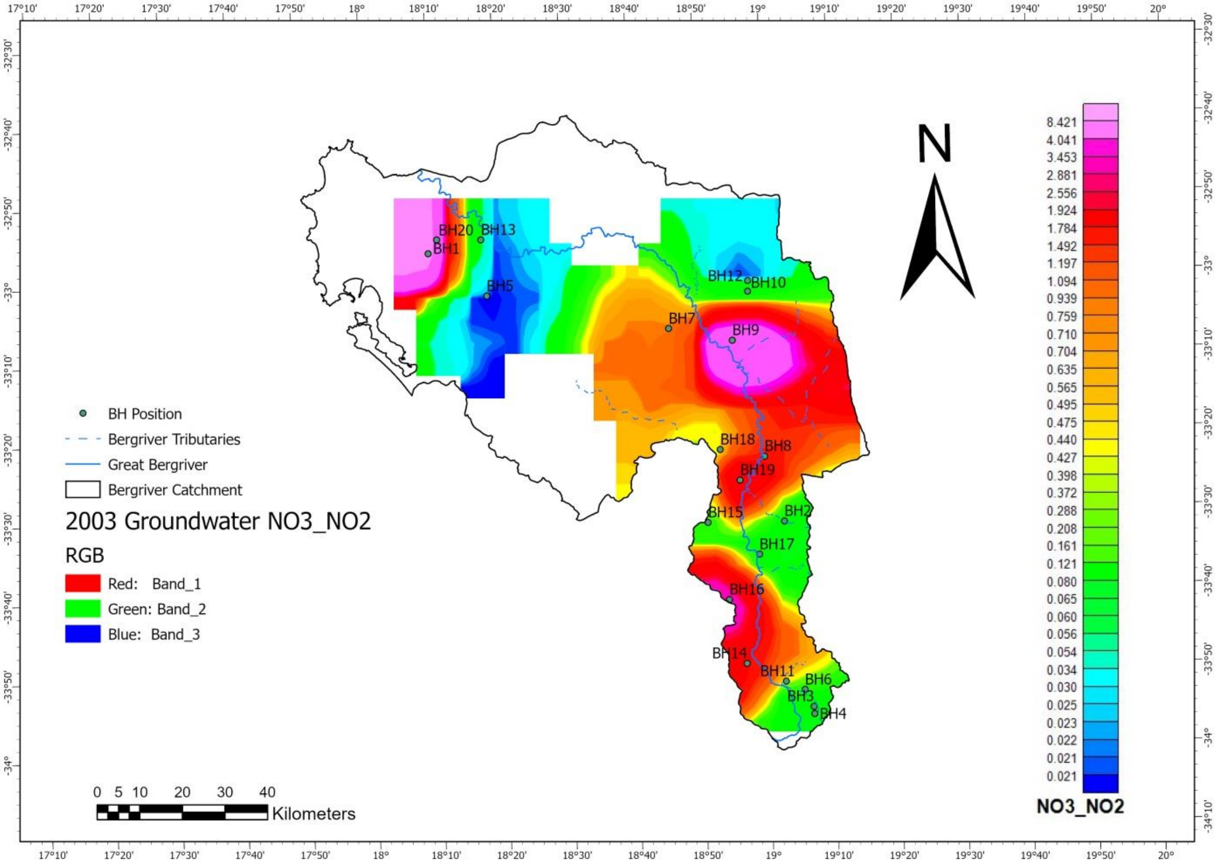

Figure 4.24: 2003 groundwater NO_3^-+NO_2^-

BH5 and BH13 also showed fluctuations of very low-low nitrate concentrations between the years 2004-2006. Figure 4.25 and 4.26 indicates that the two boreholes have similar data in 2004-2005 with the lowest values of 0.02mg/L. Furthermore, BH5 maintained the same value of 0.02mg/L throughout 2003-2006. On the other hand, BH13 had a slight increase from 0.02mg/L to 0.041mg/L in 2006.

The data for BH7 in 2003-2006 showed a decrease in concentrations from 0.7mg/L in 2003 to 0.4mg/L in 2006. BH12 however, indicated consistency between 2003-2004 with nitrate values of 0.02mg/L but showed a slight increase of 0.04mg/L in 2006 while BH10 which is in the same vicinity indicated an increase from o.02mg/L in 2003 to 0.055mg/L in 2004-6. Further upstream are BH8 and BH19 which indicated varying nitrate concentrations in which BH19 recorded fluctuations of high and low values throughout the four years displayed in Figure 4.24-4.27. BH19 only had low values in 2003 but the values increased with years particularly in 2005, whereas BH8 showed decreasing values with the years.

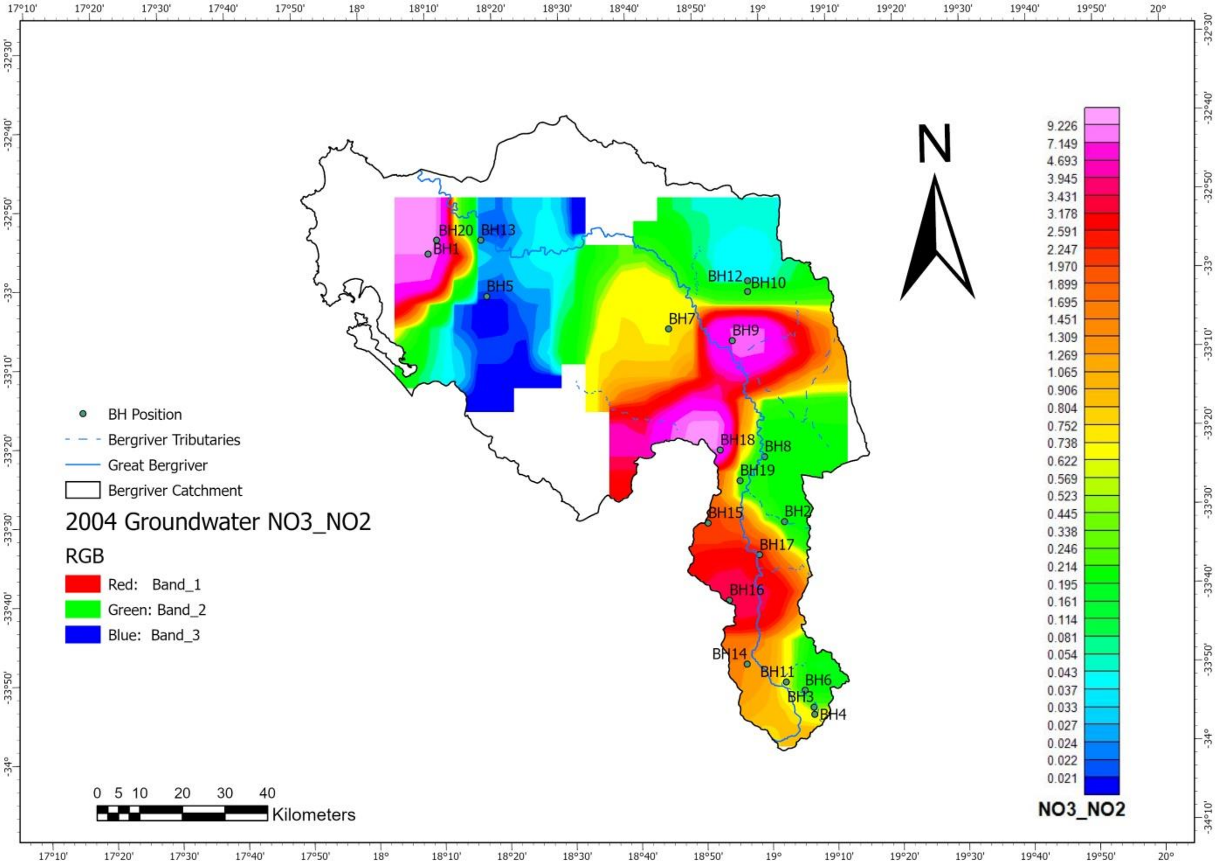

Figure 4.25: 2004 groundwater NO_3^-+NO_2^-

A little upstream of BH8 and BH19 are BH2, BH15 and BH17 which illustrated an increase in four consecutive years from 2003-2006 in Figure 4.24-4.27. The said borehole data recorded low concentrations in 2003 but slightly increased with the years from 2004-2006 although BH17 had declined concentrations in 2006. Furthermore, BH14 had decreasing nitrate concentrations from 2003 which was the highest with 1.8mg/L to 1.5mg/L in 2006. BH16 however, had values increasing only between the years 2003-2004, then declined in 2005 and drastically increased again in 2006 with the value of 5.813mg/L. BH3, BH4 and BH6 are situated at the headwaters and have low nitrate concentrations however; BH3 recorded the high value of 2.564mg/L in 2004. Nonetheless, all boreholes had nitrate values less than 1mg/L which is the permissible limit for drinking water set by SANS 241-1.

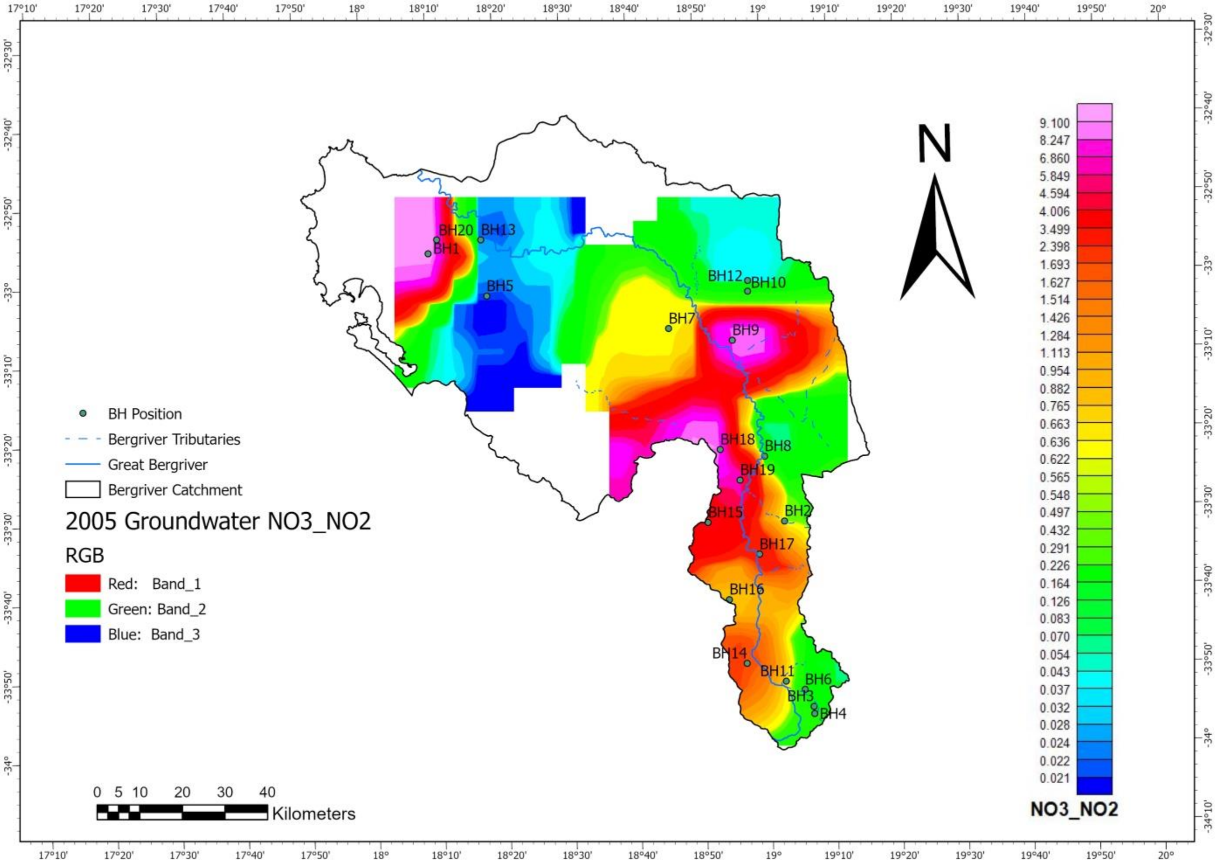

Figure 4.26: 2005 groundwater NO_3^-+NO_2^-

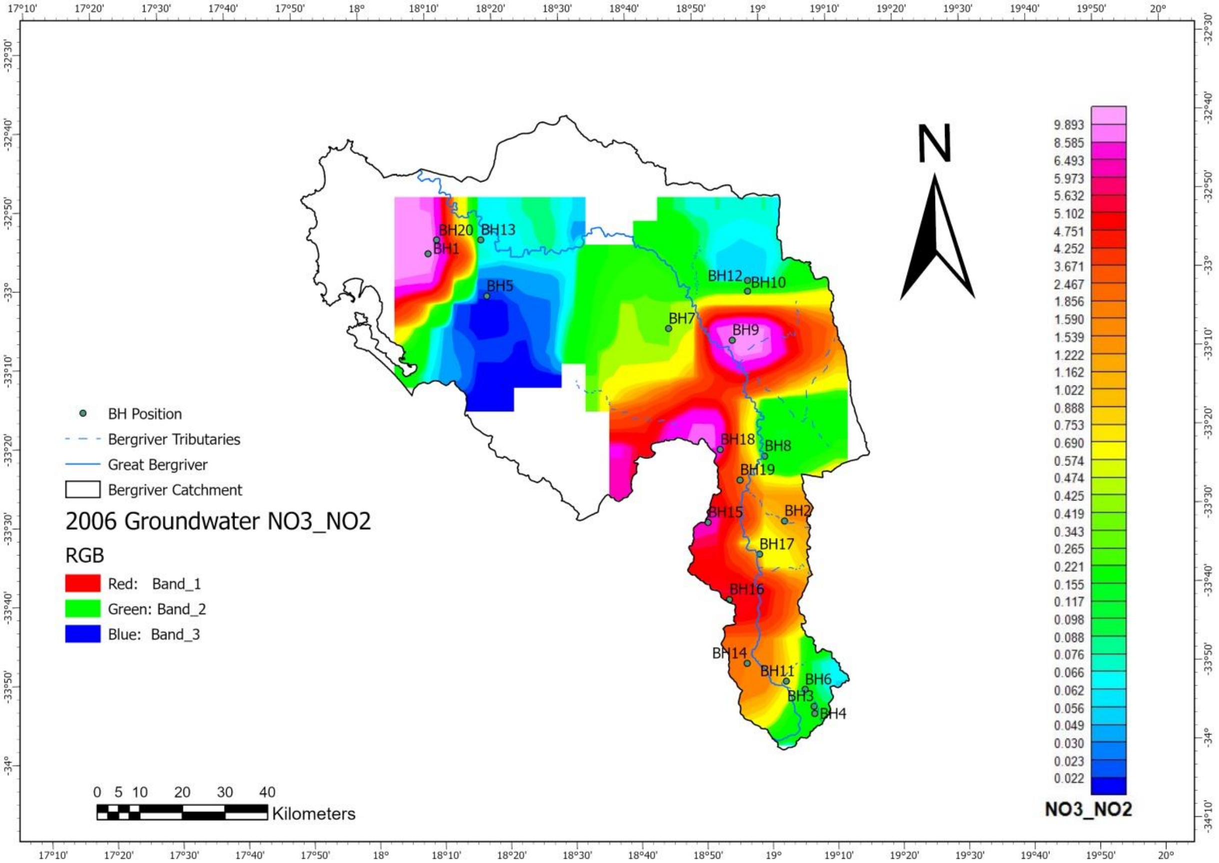

Figure 4.27: 2006 groundwater NO_3^-+NO_2^-

2007-2010 groundwater nitrates data

Figure 4.28 and 4.29 illustrates that the nitrates in 2007-2008 maintained the high vales in boreholes BH1, BH9, BH18 and BH20. The trend is similar to that of the previous four years however; the 2009 and 2010 data in Figure 4.30 and 4.31 indicated a decrease of nitrates in BH1 and BH9 respectively and notably BH9 falls within the permissible drinking standards according to SANS 241-1. Correspondingly, the other three boreholes have decreased concentration of nitrates, they are however not compliant with nitrates standards. BH20 has thus far recorded the highest nitrates concentration since 2003, with the value of 22.112mg/L in 2008 and the lowest of 11.086mg/L in 2006. Although BH1, BH9 and BH18 have been recording high concentrations in comparison to the rest of the boreholes, they have however been fluctuating between 0.06mg/L and 11.36mg/L.

moreover, with regards to the four boreholes mentioned above, there is no established trend between 2003 and 2010 with regards to nitrate concentrations.

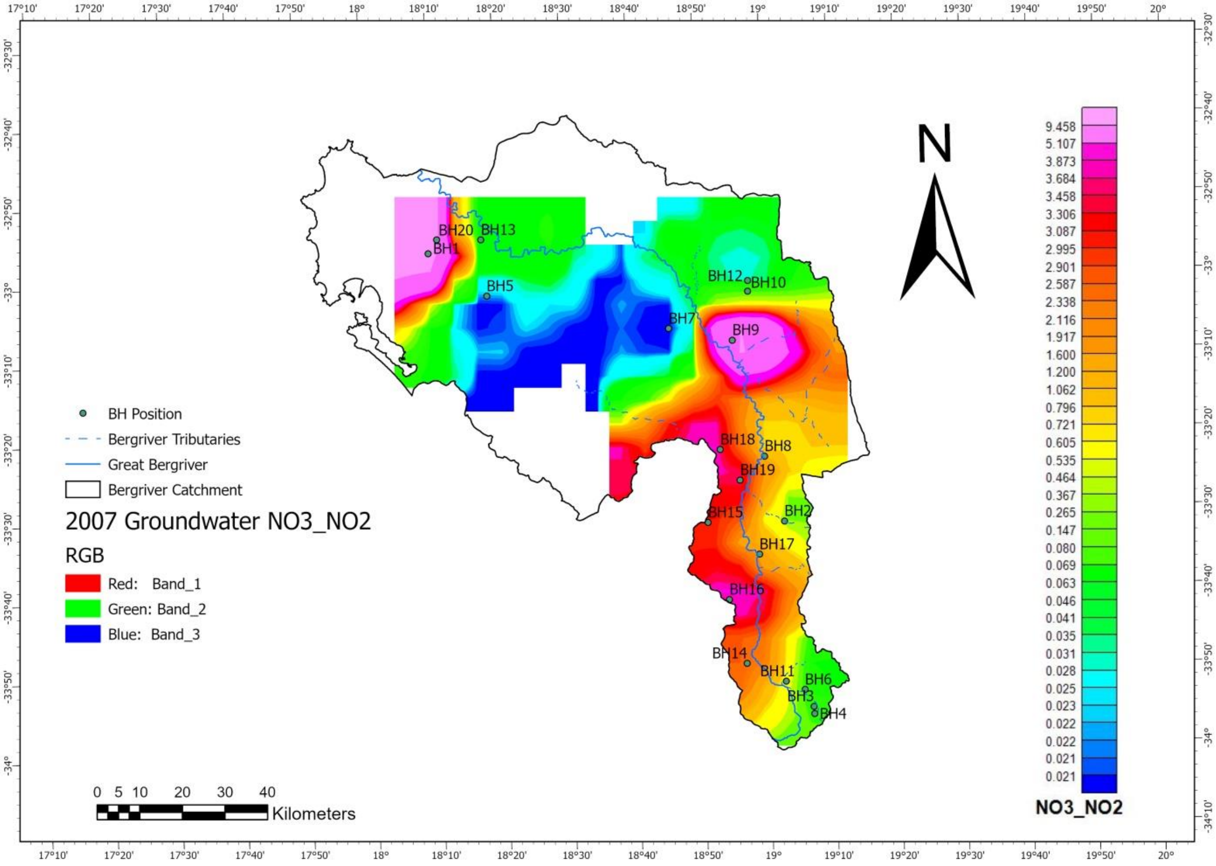

Figure 4.28: 2007 groundwater NO_3^-+NO_2^-

BH5 has shown some consistency with its nitrate concentrations between 2003 to 2008 and 2010, only in 2009 this boreholes had shown minor increase though still within permissible nitrates limits for drinking water standards. On the other hand, BH7 nitrate values have shown a decrease between 2007-2010 shown in Figure 4.28-4.31 with values not more than 0.06mg/L, contrary to the 2003-2006 dataset which had values ranging between 0.4mg/L to 0.7mg/L. Furthermore, BH10 also had shown consistency with nitrate values of 0.04mg/L in the years 2007-2010. These values have been a minor decline from the 2003-2006 data. Moreover, BH12 had shown similarities with those of BH10 such that BH12 also recorded nitrate values of 0.04mg/L in the years 2008-2010 which were a minor increase from 0.02mg/L in 2007. Overall, the nitrate values of 2007-2010 did not vary much from those of 2003-2006 in BH5, BH7, BH13, BH10 and BH12.

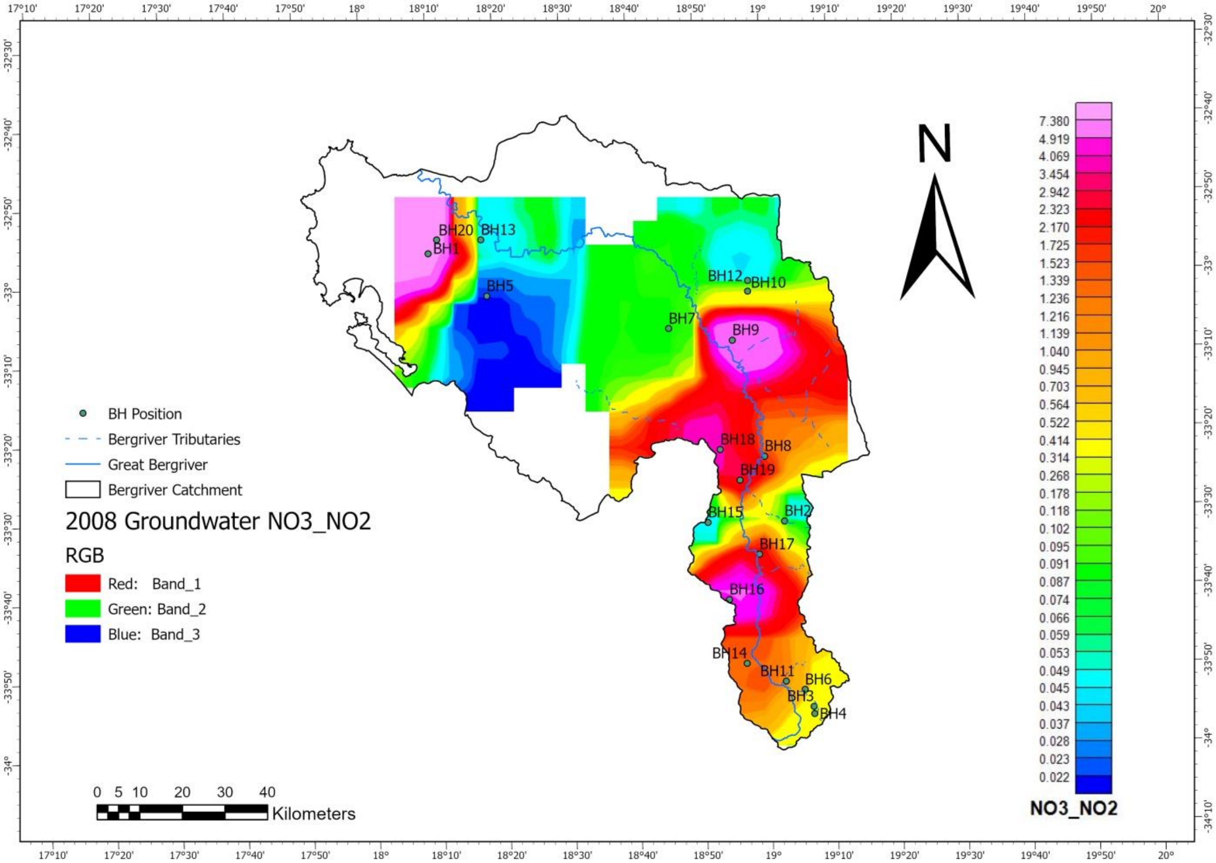

Figure 4.29: 2008 groundwater NO_3^-+NO_2^-

BH8 indicated major nitrates increase between 2007 and 2010 with values ranging between 0.68mg/L to 6.668mg/L respectively. The data between 2003 and 2006 had rather lower values; therefore an increasing trend is established. On the other hand, BH19 has not shown any form of nitrate trend. Of the eight years period discussed thus far, BH19 recorded its highest nitrate value of 7.979mg/L in 2005. The values between 2007 and 2010 are a little higher than those in 2003, 2004 and 2006 though it cannot be said there is a trend.

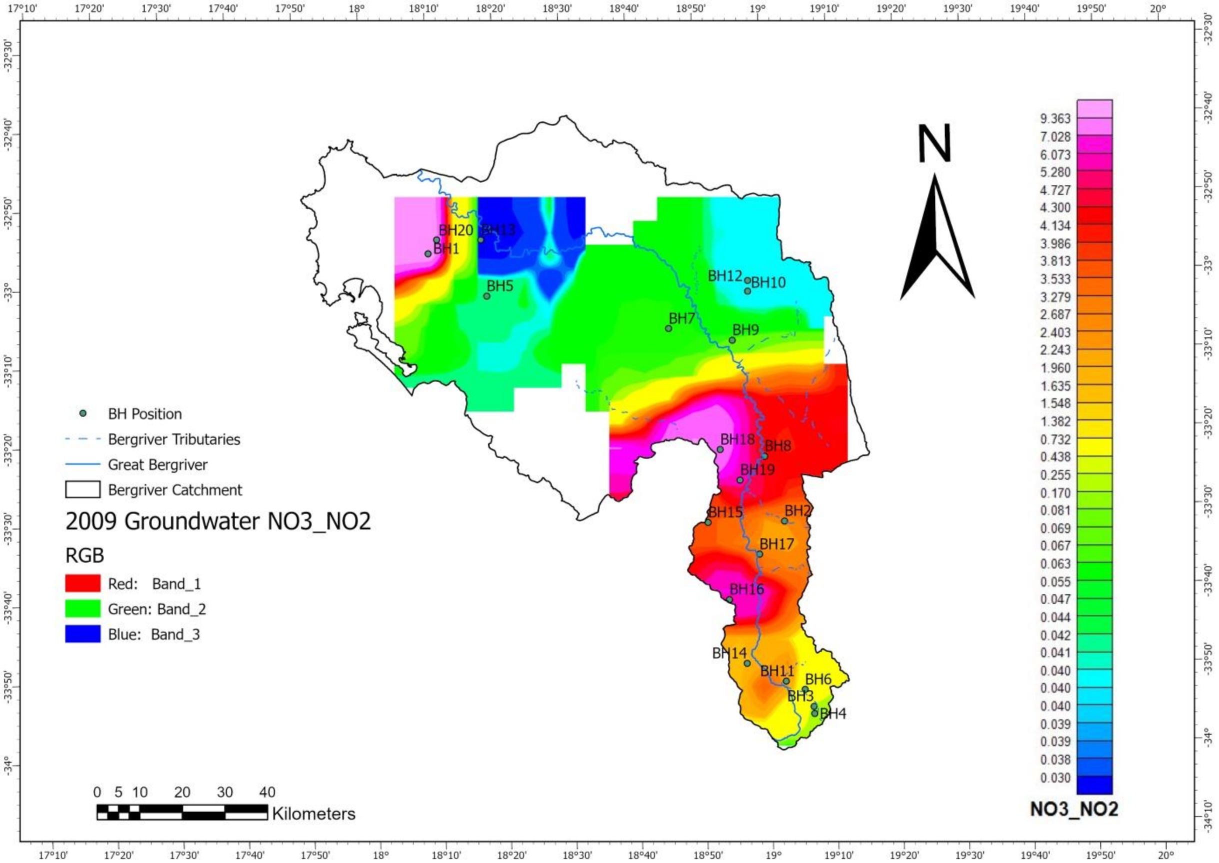

Figure 4.30: 2009 groundwater NO_3^-+NO_2^-

The nitrate data for BH16 had no particular similarities however, between 2007 and 2010 the concentrations are fluctuating with slightly higher values than those of 2003 and 2006. Similar to BH16, the data for BH11, BH14, BH17 and BH15 showed no particular similarities as it fluctuated between the high and low values from year to year. On contrary, BH2 nitrates concentrations declined between 2007 and 2010 as compared to its values in 2003-2006 data.

Although BH3, BH4 and BH6 are in the same vicinity, they however do not record similar nitrates concentrations. BH4 and BH6 recorded the lowest values of less than 1mg/L since 2003 to 2010. Contrary to BH3 which had low values though recorded one outlying value of 2.564mg/L in 2004. Of the three boreholes however, none had indicated a particular trend.

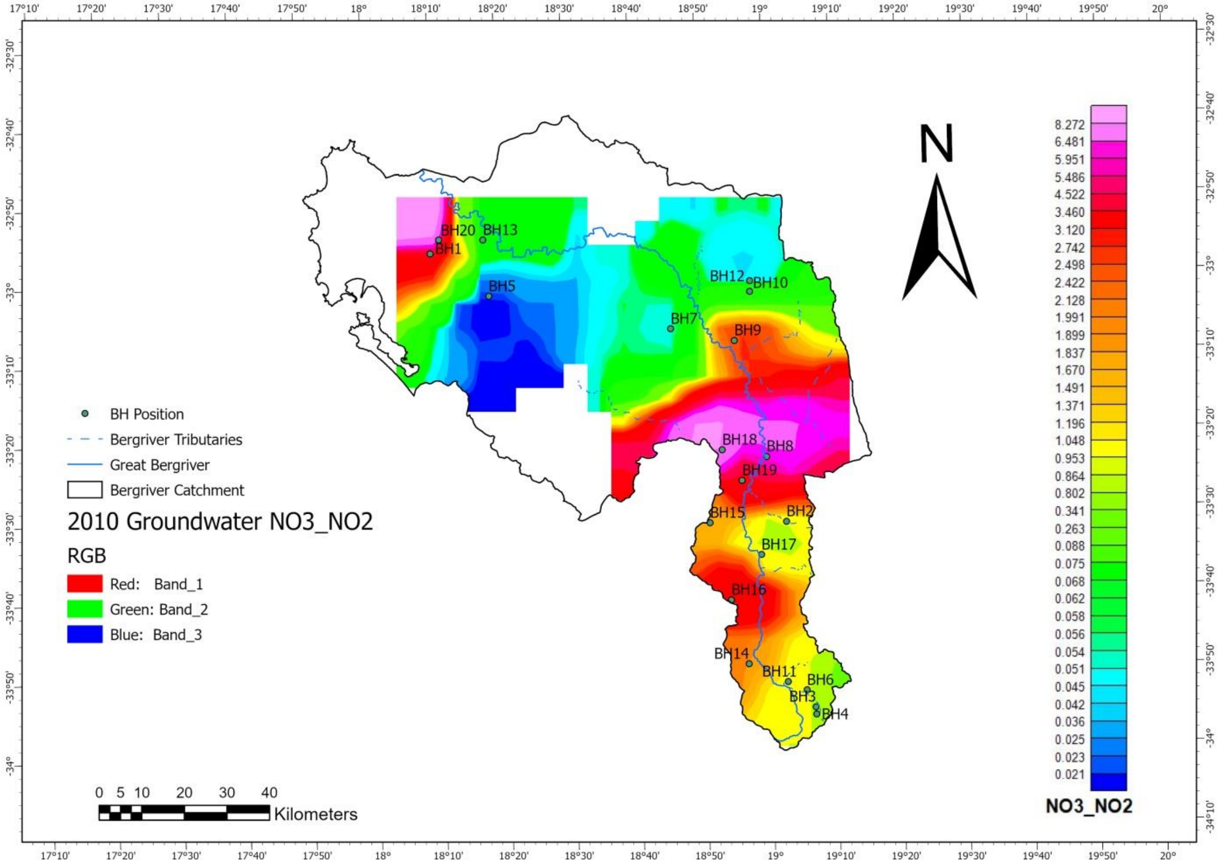

Figure 4.31: 2010 groundwater NO_3^-+NO_2^-

2011-2013 groundwater nitrates data

BH20, BH1, BH9 and BH18 maintained the trend of high values. BH20 remain the borehole with the highest nitrate concentrations of all other 19 boreholes. BH1 have however shown a drastic decline in nitrate concentrations in 2013 (Figure 4.34) with the value of 0.225mg/L. BH1 have maintained high nitrate values ranging between 2.5mg/L and 11.36mg/L since 2003 to 2012 however decline to below 0.5mg/L in 2013. Similarly, BH9 have also shown another low value of 0.22mg/L in 2013. Since 2003, BH18 had recorded its highest nitrate concentration in 2011 with the value of 16.821mg/L and the lowest of 0.354mg/L. therefore, as of 2004 BH18 has not been compliant with nitrate values regarding drinking water standards.

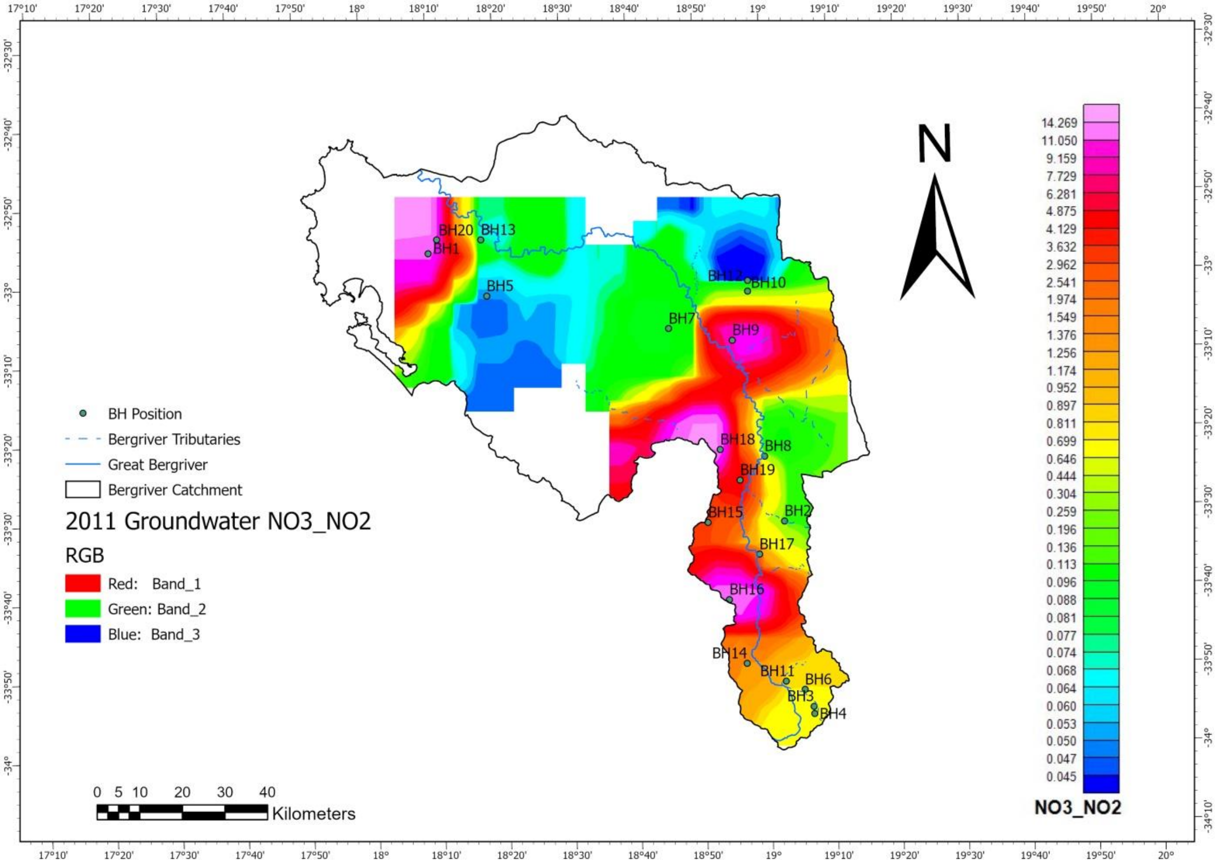

Figure 4.32: 2011 groundwater NO_3^-+NO_2^-

Furthermore, BH5 have shown consistency of low nitrate concentrations. Most years, BH5 recorded the value of 0.02mg/L and only in 2013 the concentrations increased to 0.05mg/L. BH7 and BH13 still have fluctuations of low nitrate values and thus shown no particular trend or major changes. Moreover, BH10 and BH12 have shown consistency of nitrate values of 0.04mg/L between 2007 and 2013 consecutively.

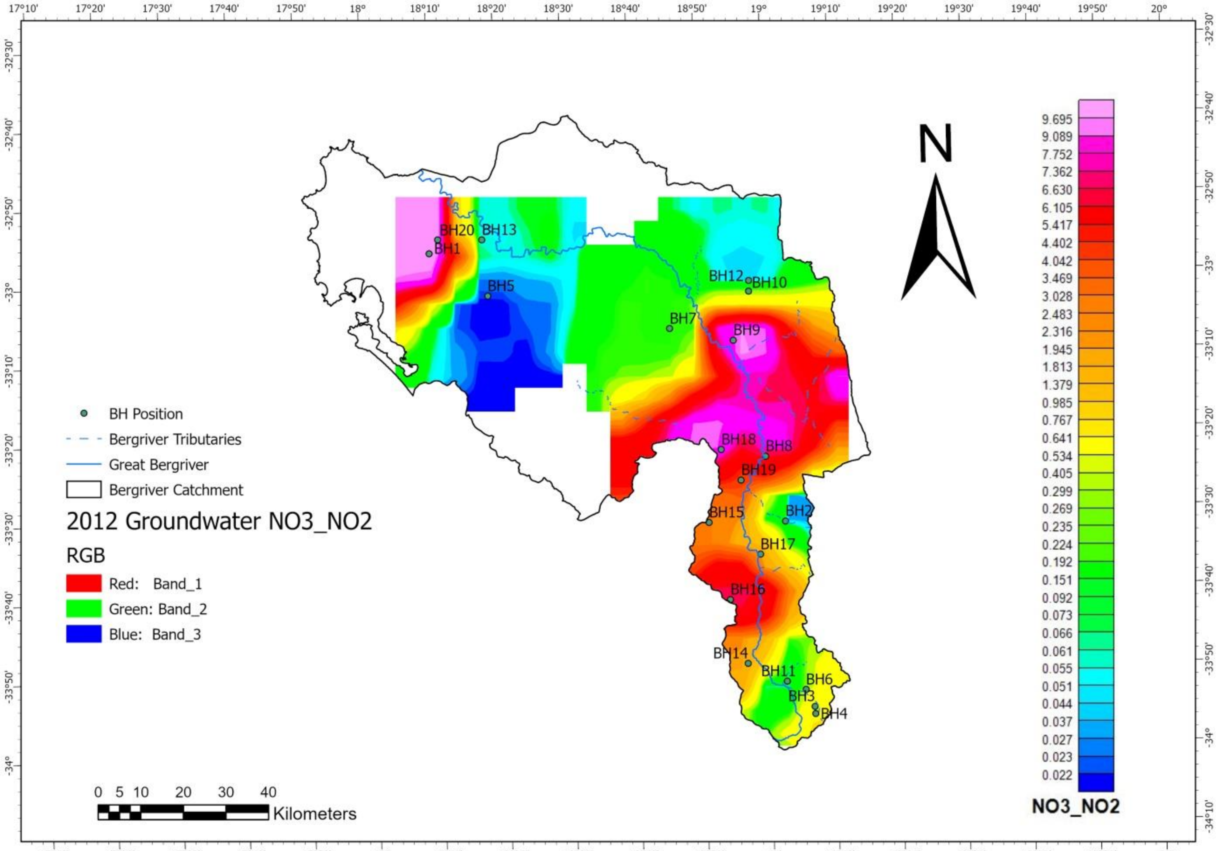

Figure 4.33: 2012 groundwater NO_3^-+NO_2^-

There was no trend or similarities established for BH8 and BH19. BH8 recorded the highest value of 8.181mg/L in 2012 and its lowest was 0.05mg/L in 2005. BH19 on the other had its highest value of 7.979mg/L in 2007 and the lowest of 0.294mg/L in 2004. Notably, since 2004 BH19 had been recording fluctuating values which were not the highest at all time but were above permissible drinking water standards. Correspondingly, BH14 had values which were not always the highest however they have been above the permissible standards except for the 2013 data which recorded 0.90mg/L. BH15 also recorded nitrate values which were mostly above the permissible limits except those of 2003 and 2008 which were 0.22mg/L and 0.04mg/L respectively. Furthermore, BH16 had no particular trend although most values were above 3.5mg/L and only in 2005 BH16 had its lowest nitrate value of 0.854mg/L.

The data for BH11 indicated lot of fluctuation of values between 1mg/L and 4mg/L however, the concentrations declined drastically from 2011-2013 (Figure 4.32-4.34) with the values below 0.05mg/L. similarly, BH2 and BH17 did not indicate any particular trend throughout the years though BH17 had several values above the permissible limits. BH3 had shown no particular trend but fluctuation of fairly low values however, 2011-2013 data shown increases as compared to other years. Furthermore, BH4 and Bh6 had maintained a trend of extremely low nitrate concentrations in which the highest value recorded for BH4 was 0.5mg/L in 2005 and the highest for BH6 was 0.8mg/L in 2011.

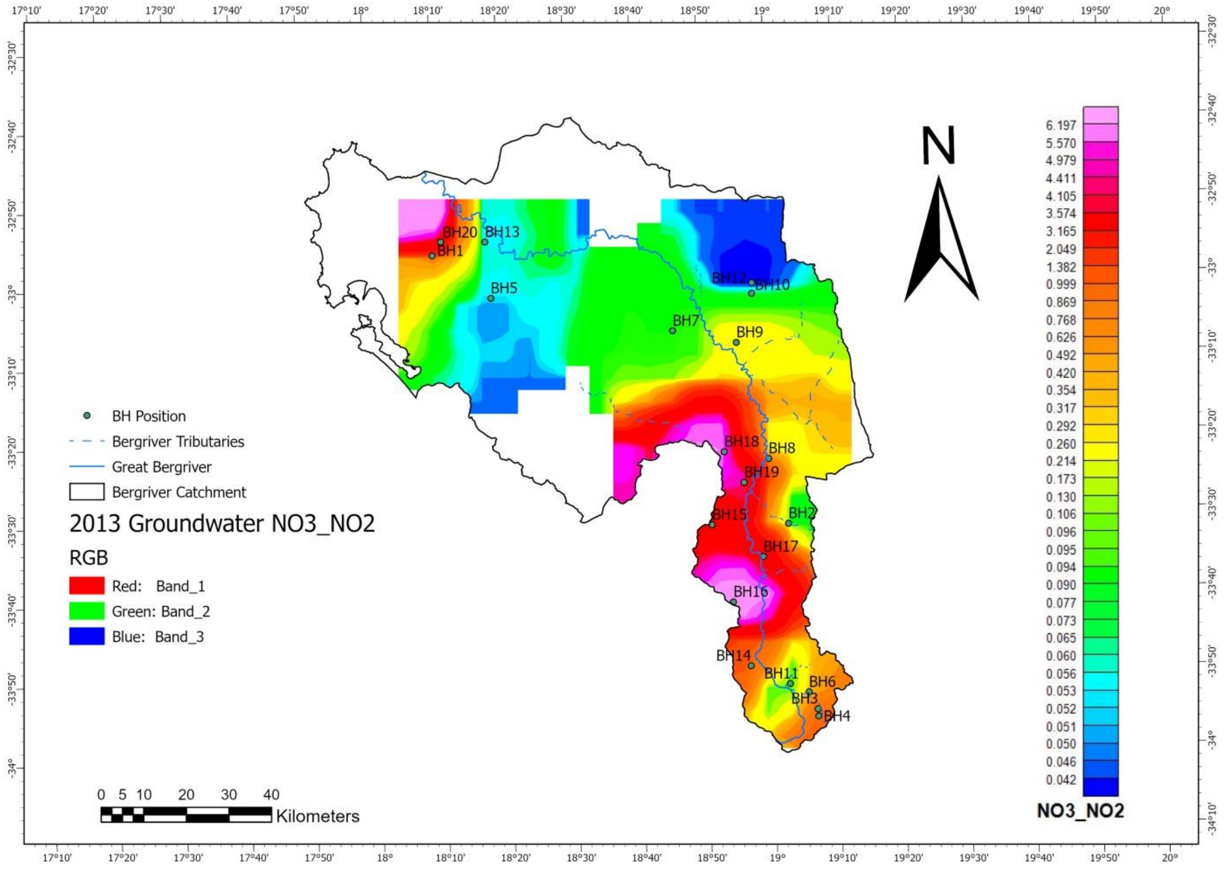

Figure 4.34: 2013 groundwater NO_3^-+NO_2^-

4.5 Surface Water NO3+NO2 variations in the BRC

Studies from Mgese (2010) and De Villiers (2007) have highlighted that nitrates have for some years become an environmental issue in certain areas of the BRC such as Mbekweni informal settlements just outside Paarl, as well as others which have ailing sewage infrastructure. Below are the results of nitrate trends obtained from the SW1-SW18 in the BRC

2003-2006 surface water nitrates data

SW17 and SW18 indicated that nitrates were extremely low at those sampling points between 2003 (Figure 4.35) and 2006 (Figure 4.36). The values were ranging between 0.04mg/L and 0.3mg/L. Similarly, SW8, SW9 and SW10 also shown very low nitrate concentrations between 2003 and 2006 with SW8 being the lowest with 0.03mg/L in 2005 shown in Figure 4.37. Although the sample points had very low value, SW10 recorded 1.02mg/L in 2005 making it one of the sample points with concentrations above permissible limits by SANS 241-1. Correspondingly, SW3 and SW16 also had low nitrates. SW3 however recorded the highest concentration of 3.51mg/L in 2005 while SW16 recorded the highest of 4.06mg/L in 2004 (Figure 4.38).

The east of SW3 and SW16 are sample points SW5, SW6 and SW7 which have shown extremely low nitrates throughout the years 2003-2006 with values ranging from 0.03mg/L to 0.1mg/L. although SW7 had such lowest values in 2003, 2004 and 2006 it recorded 2.33 in 2005 making it the second highest in 2005. SW11 began with the value of 1.mg/L in 2003 but declined in 2004 and 2005 then increased again to the value of 1.3mg/L in 2006. SW13 had low nitrate concentration in 2003 however increased throughout 2004-2006 with values above the permissible limits for drinking water standards.

Contrary to all the other mentioned sample points, SW14 had shown a chronological increase throughout 2003-2006 wherein this sample point recorded the higher nitrate value of 2.46 in 2006. SW15 however had shown fluctuations of high and low values such that there was no particular trend. The values varied between 0.09mg/L and 3.5mg/L in no particular order between 2003 and 2006. East of SW14 is the sample point SW2 which had shown fluctuation of very low values ranging between 0.04mg/L ad 0.33mg/L in no particular trend.

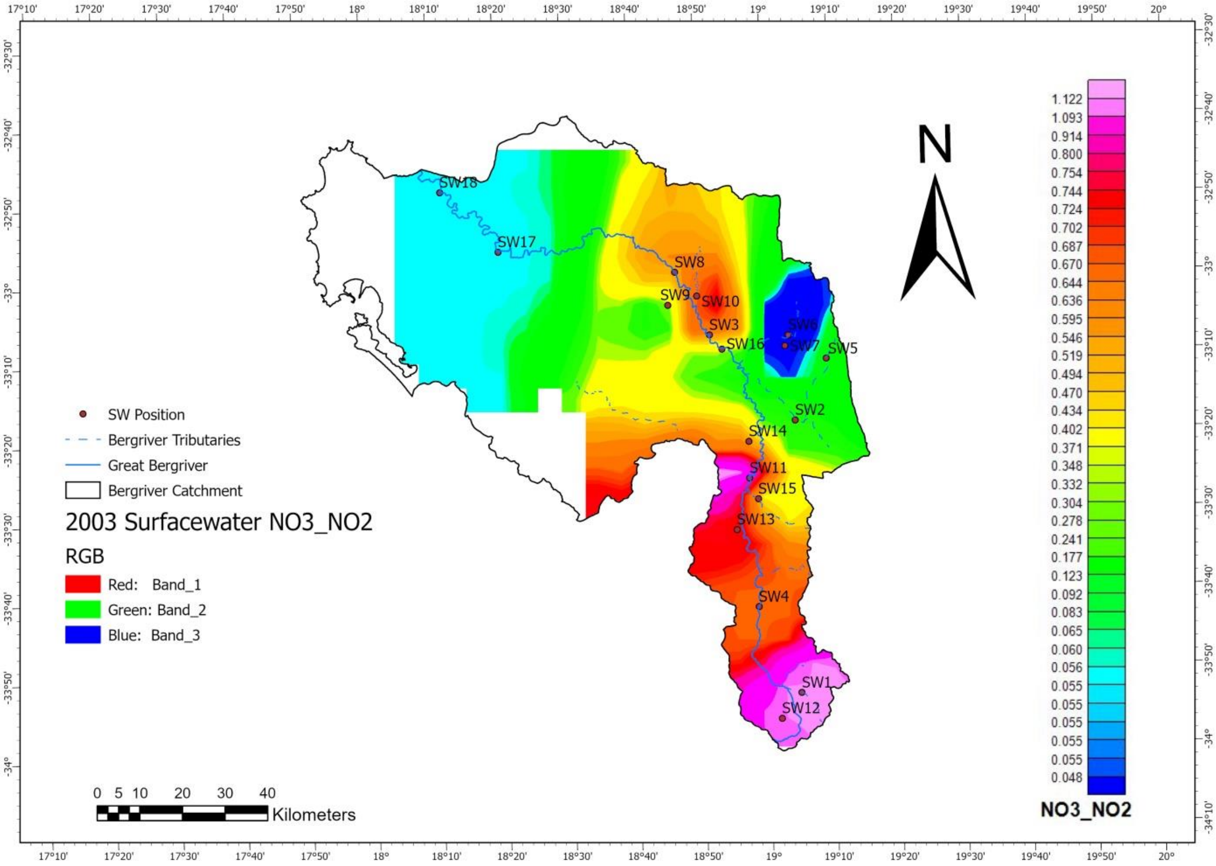

Figure 4.35: 2003 surface water NO_3^-+NO_2^-

SW4 showed consistence of nitrate values of 0.6mg/L in 2003 and 2004 however recorded an increase of 1.5mg/l in 2005 then decreased again in 2006. Similarly, SW1 and SW12 had no specific trend but variation of high and low concentrations. Nonetheless, SW1 recorded a high of 1.1mg/L in 2003 and 2006 whilst SW12 had 1.02mg/L in 2003 and 2.13mg/L in 2005.

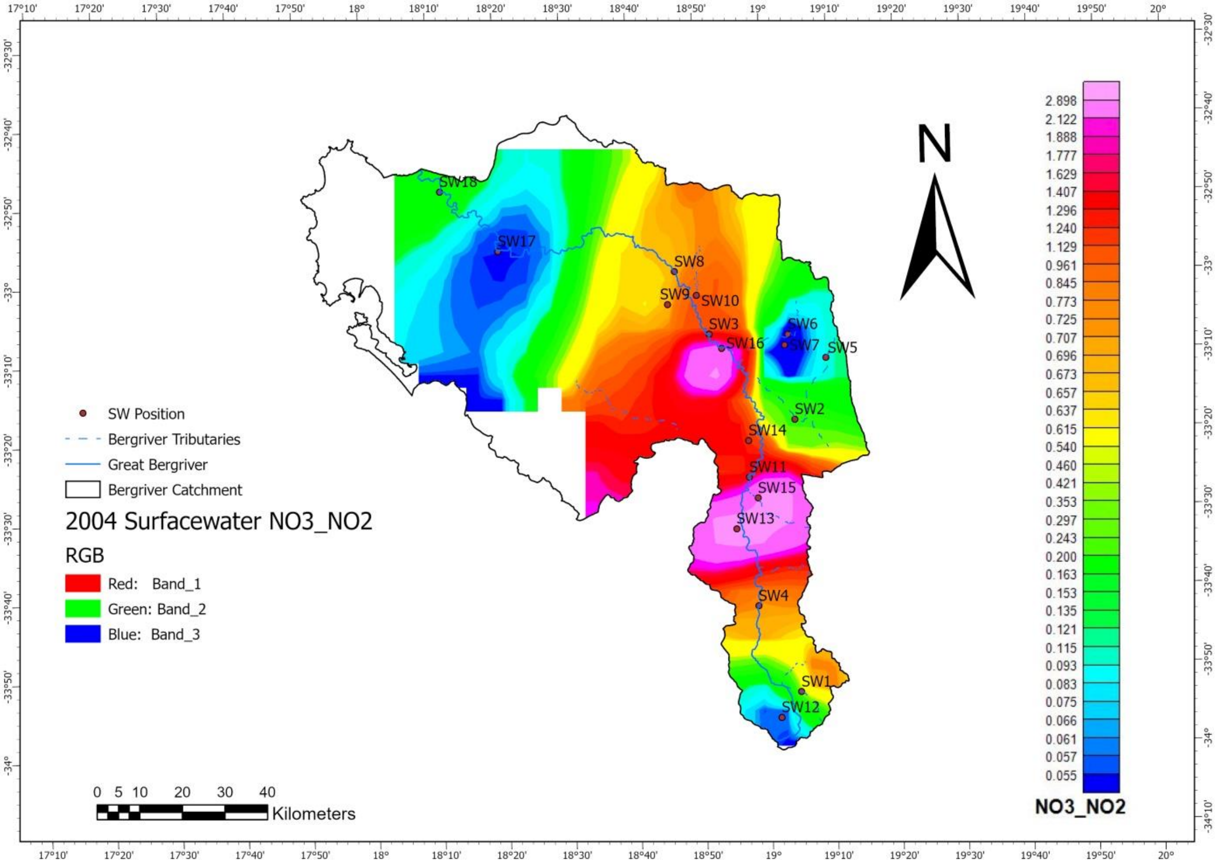

Figure 4.36: 2004 surface water NO_3^-+NO_2^-

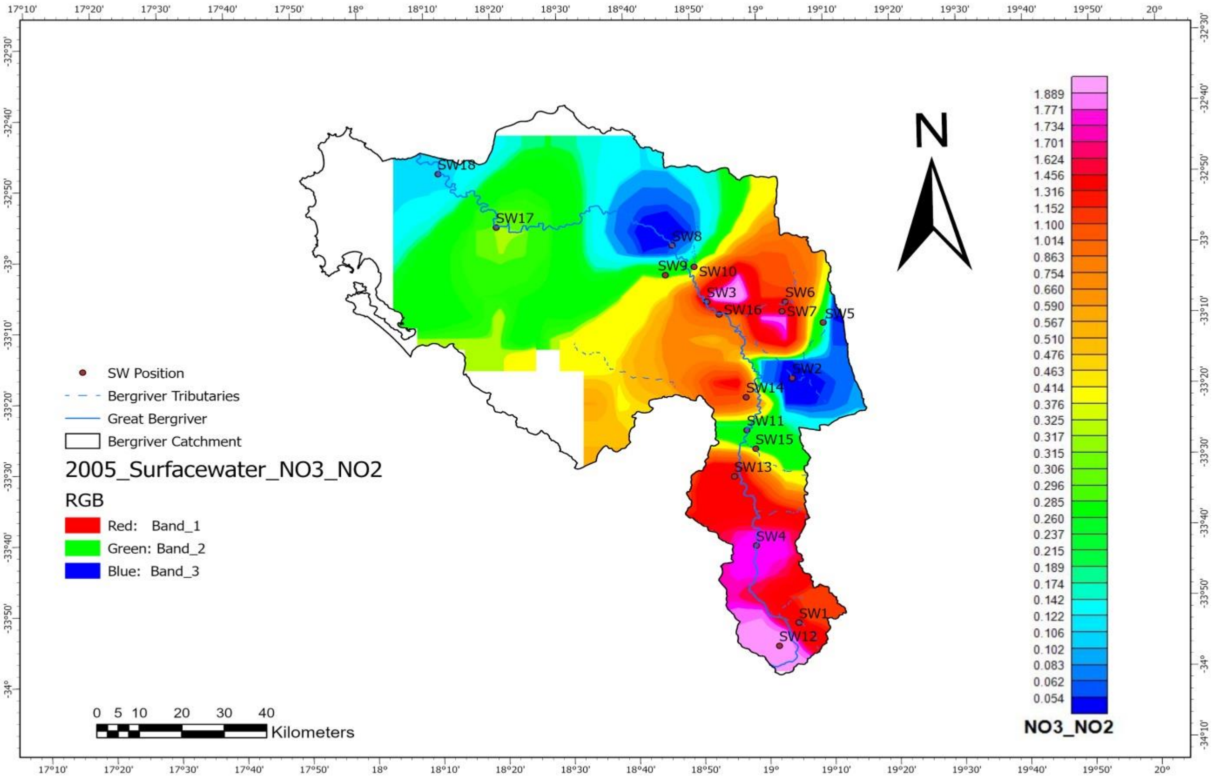

Figure 4.37: 2005 surface water NO_3^-+NO_2^-

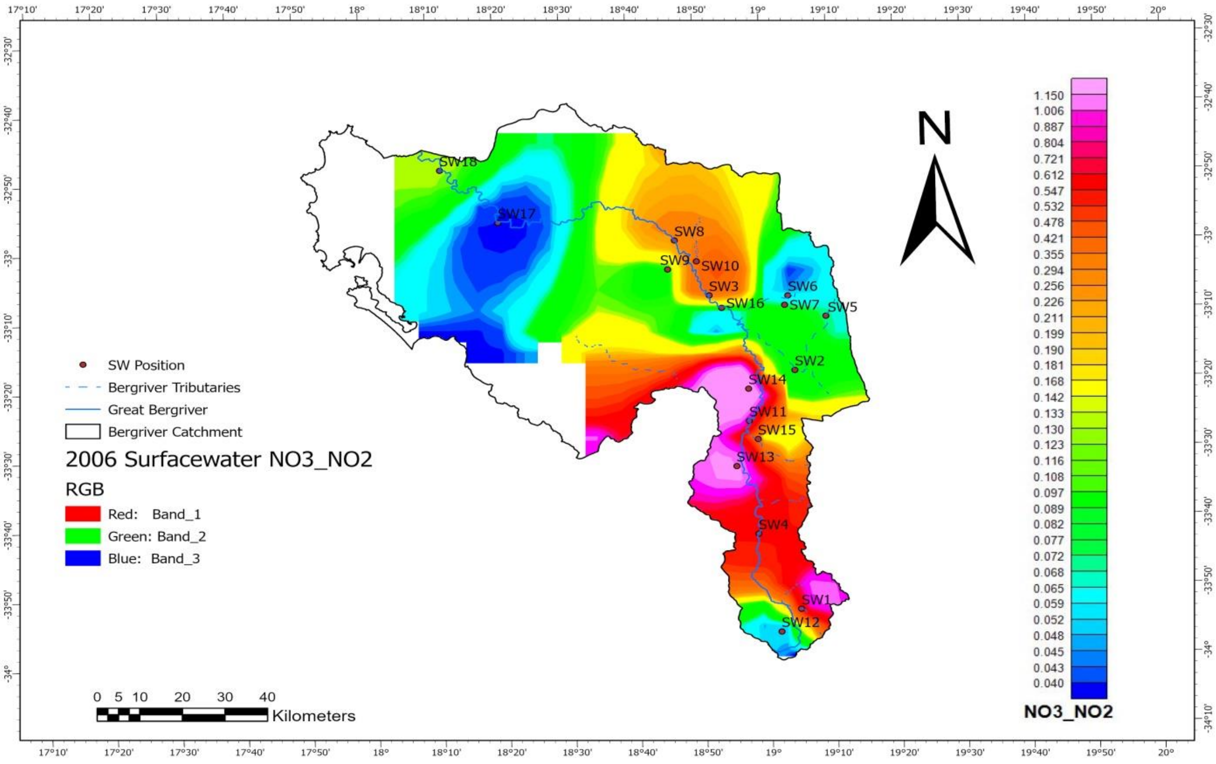

Figure 4.38: 2006 surface water NO_3^-+NO_2^-

2007-2010 surface water chemistry data

Although SW17 and SW18 had shown consistency with low nitrate concentrations, SW17 however recorded its first high nitrate above permissible limit with the value of 1.9mg/L in 2007 (Figure 4.39). Nonetheless, SW18 maintained the consistency of low nitrate values. Similarly, SW8 also maintained low values of less than 1mg/L since 2003 to 2010 (Figure 4.42). Furthermore, SW9 also maintained low nitrate values between 2003 and 2009. In 2010 however the values increased slightly to 1.2mg/L which was its first high value since 2003. With regards to SW10, an increase can be observed from 2008-2010 (Figure 4.40-4.42) contrary to the 2003-2006 data which had very low values.

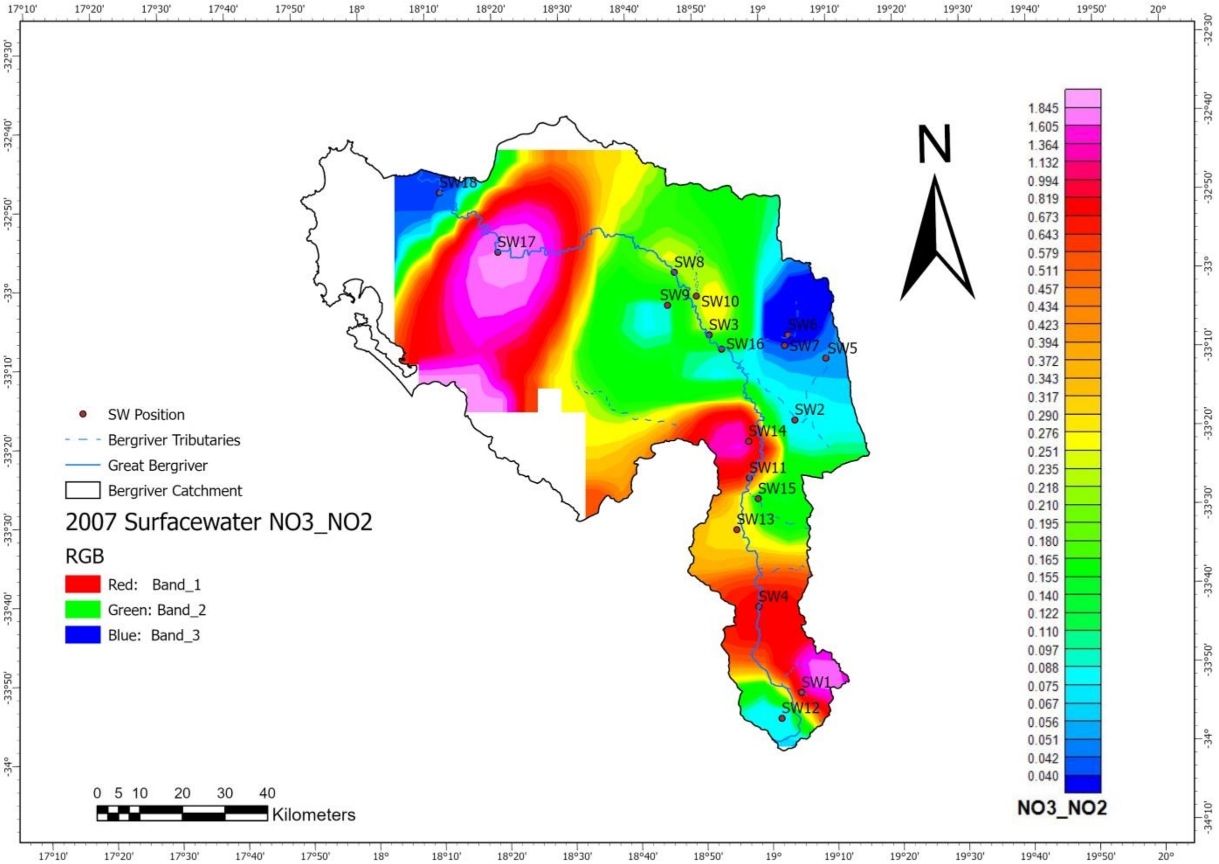

Figure 4.39: 2007 surface water NO_3^-+NO_2^-

Furthermore, SW3 had shown that the nitrates at this sample point had maintained consistency of very low values below 1mg/L since 2003-2010. On the other hand, SW16 had shown a moderate increase in 2010 with the value of 1.6mg/l which was its second higher value since 2004. Thus far SW5, SW6 and SW7 maintained low values since 2003-2010. The values for 2007-2010 range between 0.02mg/l and 0.06mg/L for all the three sample points. SW2 nitrate concentrations range between 0.07mg/L and 0.3mg/L in 2007-2010 dataset, showing no increment thus far. On the other hand, SW11 had shown consistency of values between 1-1.2mg/L in 2008-2010 however, 2007 data showed low nitrates.

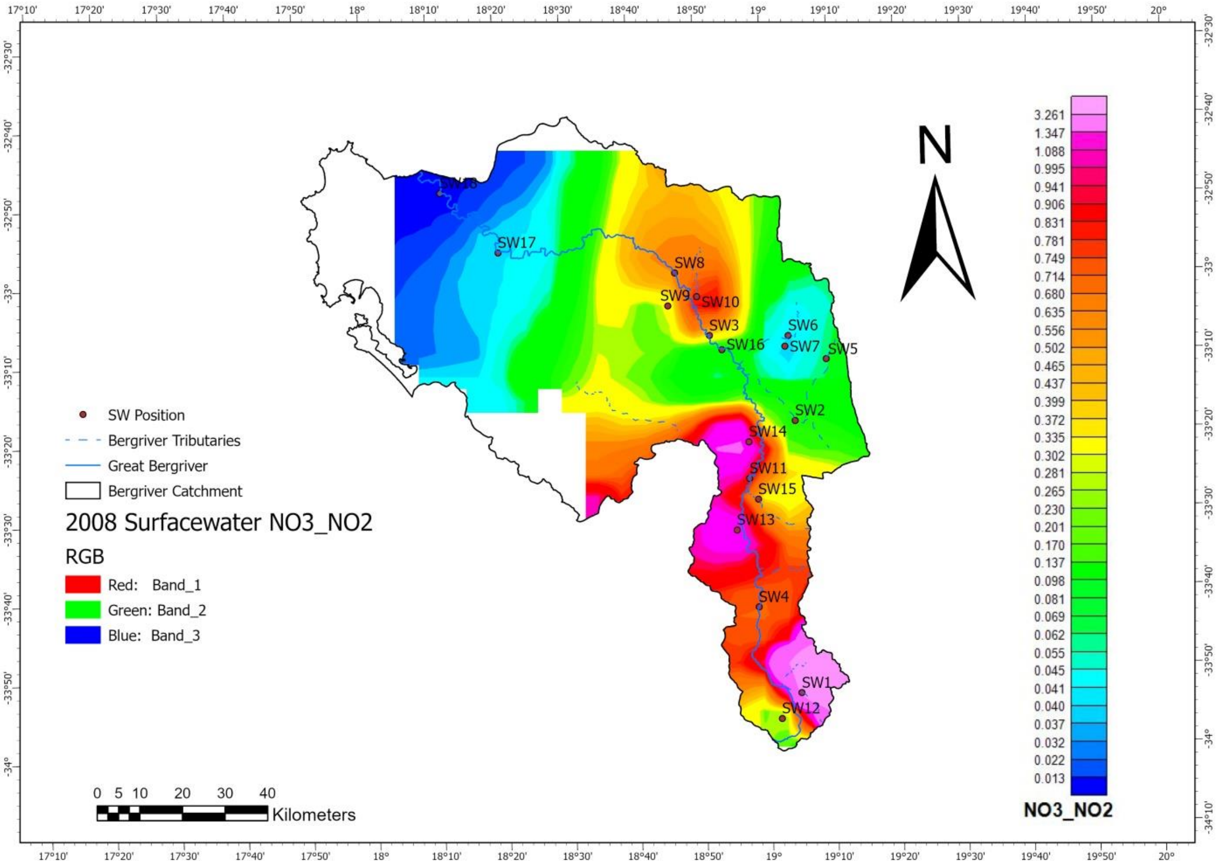

Figure 4.40: 2008 surface water NO_3^-+NO_2^-

Notably, SW13 showed an increase of nitrates in 2008-2010 in no particular order. Similar to the 2003-2006 dataset, the increment occurred for three consecutive years wherein the fourth year records low values. Additionally, SW14 nitrate values have been above 1.2mg/L since 2004. Therefore, a trend of high value is observed. Contrary to SW14, SW15 indicated a trend of very low nitrate concentrations throughout 2003-2010; only in

2005 there was a slight increase. Nonetheless, the values between 2007 and 2010 were ranging between 0.08mg/L and 0.3mg/L.

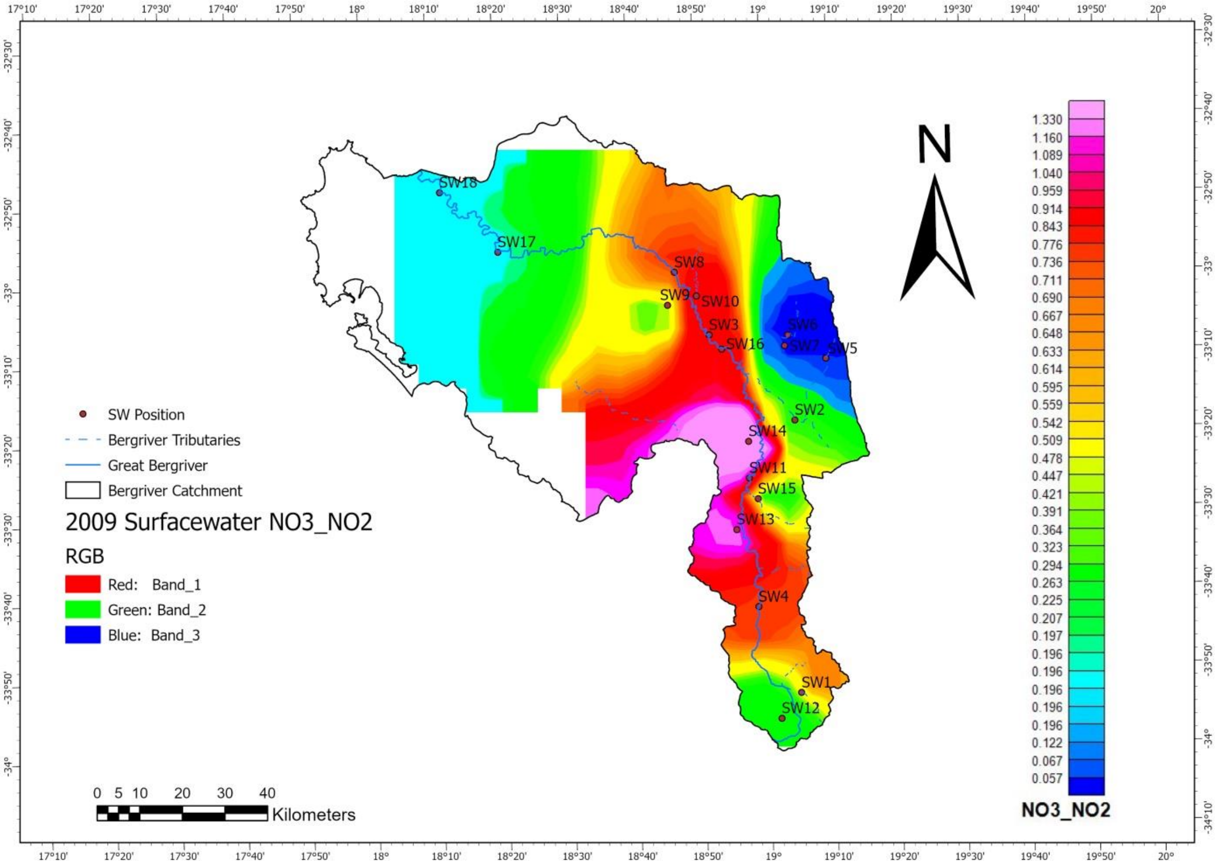

Figure 4.41: 2009 surface water NO_3^-+NO_2^-

The nitrates concentrations of sample point SW1 vary between the high and the low values. Similar to the 2003-2006 dataset, the 2007 -2010 also had variations of highest and lowest values. SW1 recorded its highest value of 8.66mg/L in 2008 and its lowest in 2009 with the value of 0.68mg/L. thus far; SW1 had the highest nitrate value of all the surface sample points. For sample point SW12, the 2007-2010 dataset showed very low values compared to the 2003-2006 dataset. In 2007-2010 the values ranged between 0.05mg/L and 0.2mg/L whereas in 2003 the values ranged between 0.03mg/L and 2.13mg/L.

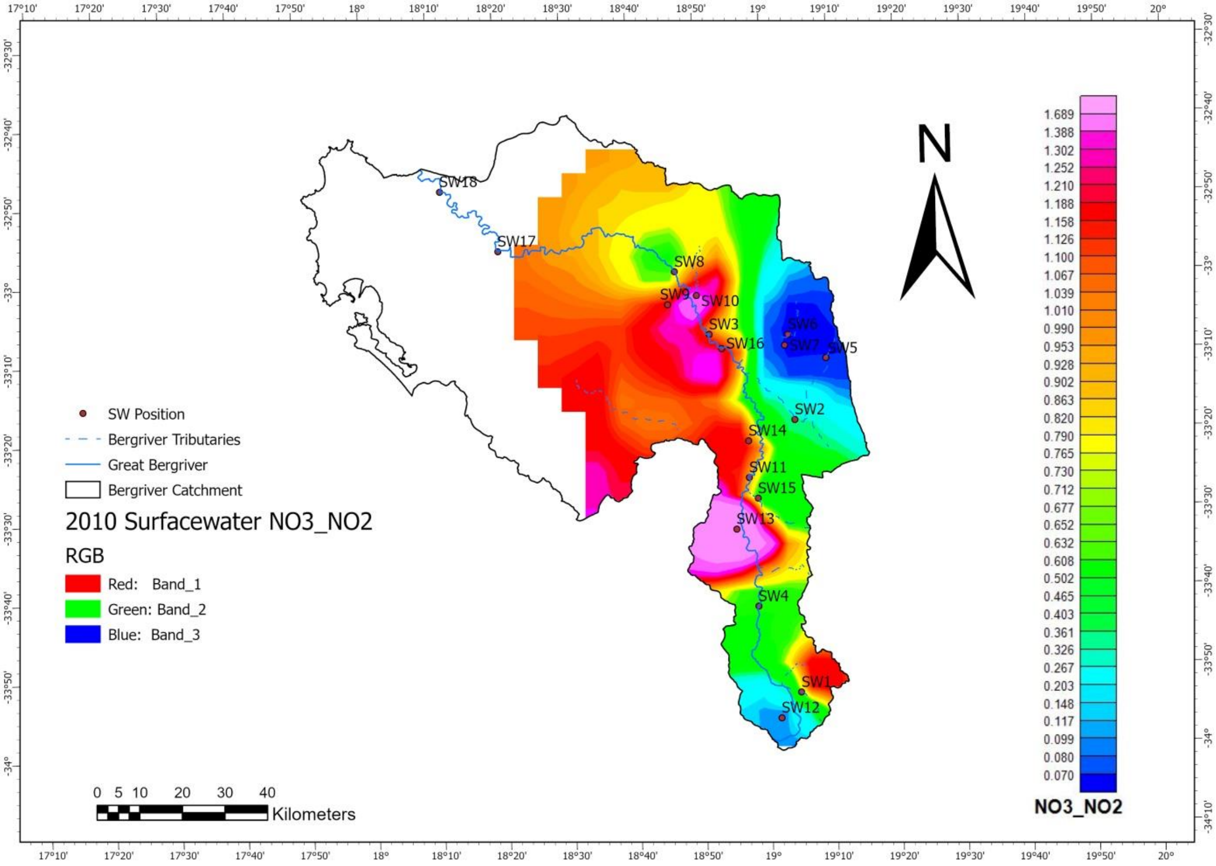

Figure 4.42: 2010 surface water NO_3^-+NO_2^-

2011-2013 surface water chemistry data

SW17 and SW18 still maintain the trend of low nitrate concentrations ranging between 0.02mg/L to 0.8mg/L from 2003-2013. Thus far, between two sample points SW17 is the only one that recorded the value above 1mg/L in 2007. Similarly, SW8 have also indicated a trend of very low values below 1mg/L between 2003 and 2012 however, in 2013 SW8 had shown an increase with the value of 1.28mg/L. In 2012 (Figure 4.44) and 2013 (Figure 4.45), SW9 had shown a drastic increase of nitrates in which the first highest value of the SW9 was recorded in 2012 with the value of 3.43mg/L. Nonetheless; SW9 had shown consistency of low values between 2003 and 2009. Additionally, Figure 4.43-4.45 shows that SW10 continues to increases in 2011-2013 with its highest value of 3.17mg/L in 2013. Furthermore, SW10 had been recording nitrate values of more than 1mg/L since 2008, as a result a trend can be observed.

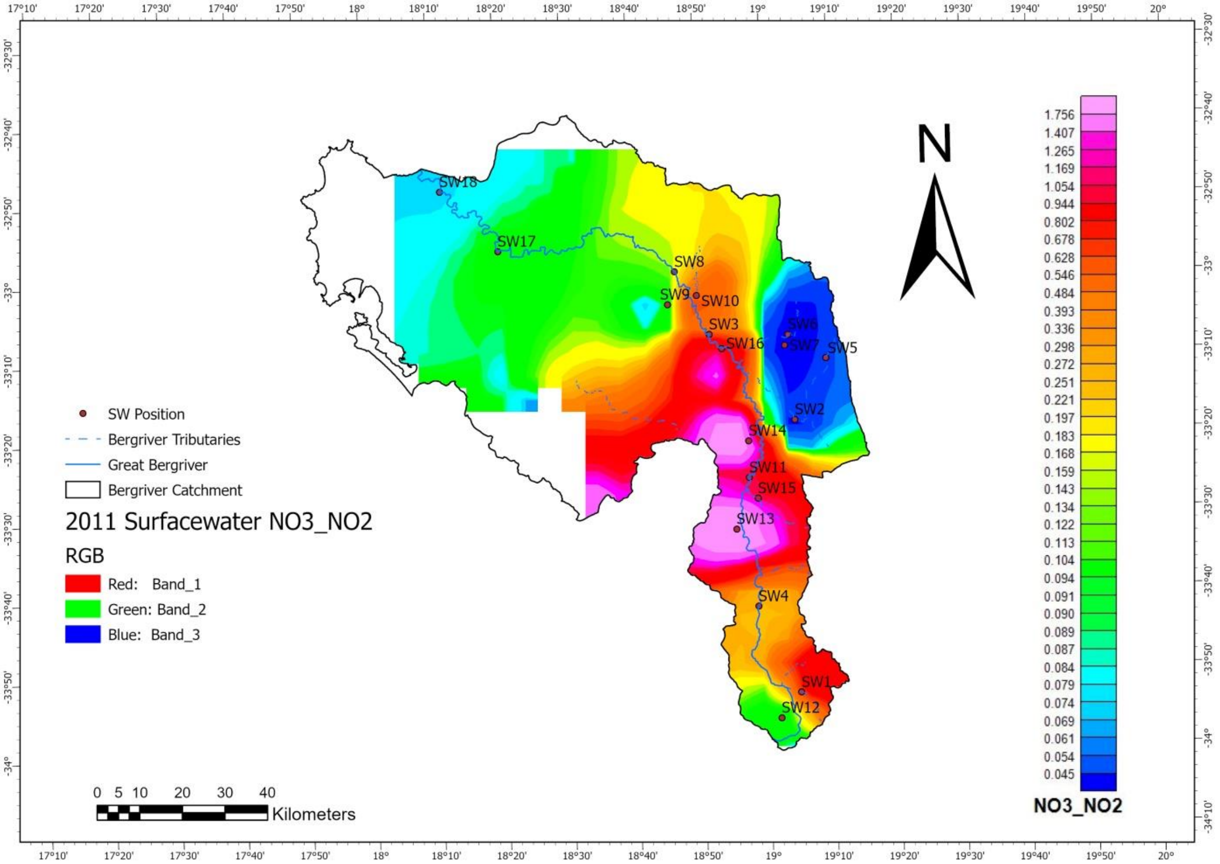

Figure 4.43: 2011 surface water NO_3^-+NO_2^-

The water quality data for SW3 indicated that the sample point only recorded its second highest nitrate value in 2013 with 1.25mg/L. Throughout 2006-2012 the values had been less than 1mg/L. On the other hand, SW16 had been showing increasing nitrates since 2010 after a fluctuation of low and high nitrate values between 2004 and 2009. Figure 4.43-4.45 indicated that the dataset for SW11 showed a slight decline in 2011 but increased again in 2012 and 2013.

SW14 showed a drastic decline in 2012 and 2013 after recording 2.93mg/L in 2011. Nonetheless, SW14 indicated a trend of high values ranging between 1.4mg/L and 2.93mg/L between 2004 and 2011. In contrast, SW15 continues to the trend of low nitrate values throughout 2003-2013. Furthermore, SW13 thus far recorded only two low nitrate values of less than 1mg/L in 2003 and 2007. All other years, SW13 sample point had been recording values more than 1mg/L.

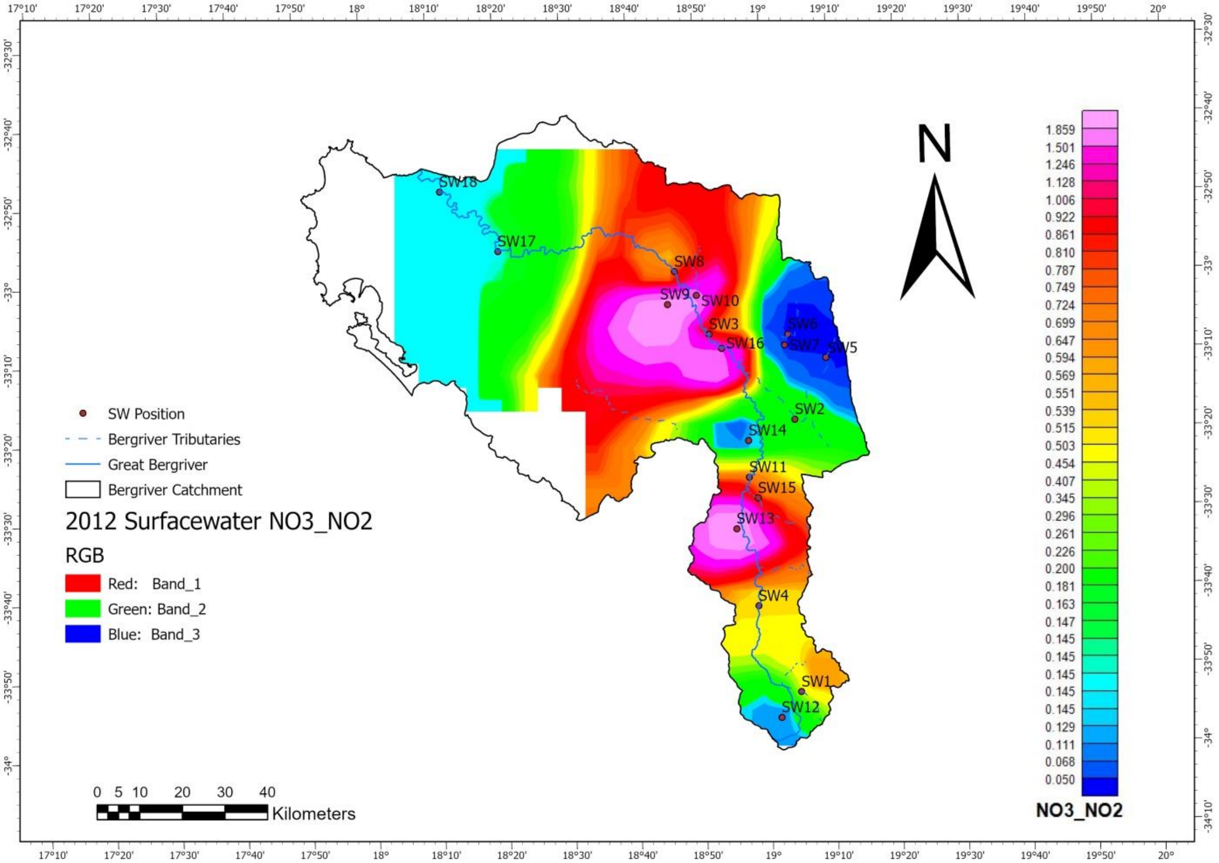

Figure 4.44: 2012 surface water $NO_3^-+NO_2^-$

SW2 continued with the trend of low values ranging from 0.04mg/L and 0.4mg/L through 2003-2013. Similarly, SW4 had also shown a trend of very low values ranging between 0.2mg/L and 0.7mg/L in 2003, 2004 and 2006-2014. Only in 2004 did the sample point record a value more than 1mg/L. In addition, SW5 also had values ranging between 0.04mg/L and 0.1mg/L throughout 2003-2013. Similar to SW5, SW6 had also been recording low values from 0.02mg/L to 0.8mg/L throughout 2003-2013. SW7 is not very dissimilar also as it had shown low values in 2003, 2004 and 2006-2013 however had a higher value in 2007.

The water quality data for SW12 also indicated that SW12 had nitrate values ranging from 0.02mg/L to 0.8mg/L since 2003 until 2013. On the other hand, SW1 continues to record the high and low values throughout the years. Only in 2013 SW1 recorded its second highest nitrate value of 5.15mg/L, nonetheless there is no particular trend.

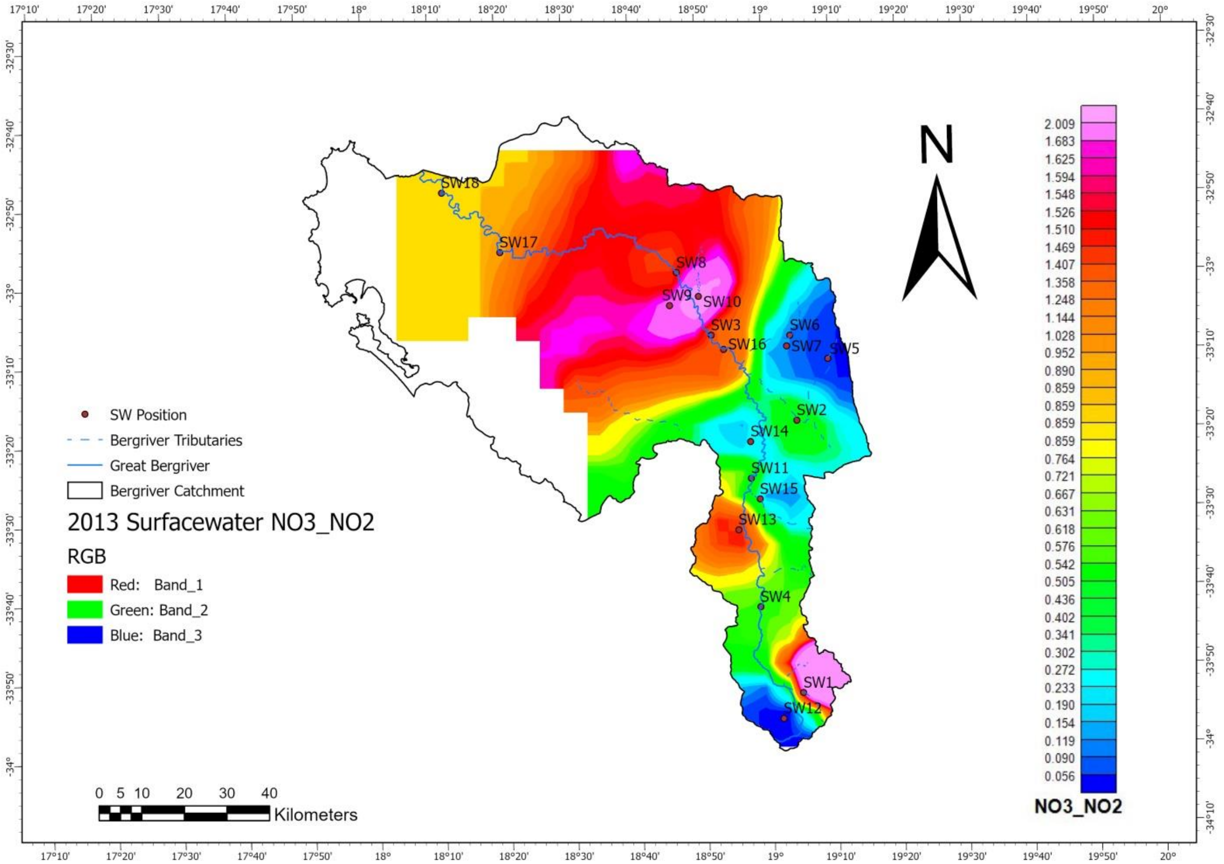

Figure 4.45: 2013 surface water NO_3^-+NO_2^-

4.6 Surface data collected in 2016

The data presented below on Table 4.3 represent the surface water data that was sampled in 2016. The blank spaces in the table below are a result of undetectable values. In comparison with the data presented above from the year 2003 to 2013, the difference in nitrates concentrations cannot be missed. From the head water where S1 and T1 are located, the nitrates concentrations are far more than those found in 2003-2013 data for both surface and groundwater. In addition, the 2016 data in terms of nitrates far exceed the values stipulated in the guidelines particularly those of drinking water standards litigated by SANS 241-1. The lowest value of nitrates in the data below is 29.9mg/l at S23 however, it still exceed the permissible limit for drinking water.

Furthermore, the last two samples, S22 and S23 have recorded high-significantly high values for all the parameters presented below. The two sample points are located near the river mouth; as a result, some parameters such as Na, Cl and Ca may have been influenced by the occurrence of sea water.

Table 4. 3: 2016 surface water sample results

Sample ID	Ca	Mg	K	Na	Cl	NO_3- +NO_2-	SO_4-
T1	6.867	2.197	1.644	11.19	10	58.3	2.1
T2	17.01	26.66	3.456	103.6	94.3	66.6	45.3
T3	6.744	9.814	1.497	61.79	57.8	57.5	4.9
S1	1.117	0.4755	1.57	3.048	3.8	55.1	
S2	1.082	0.4722	0.2583	3.131	2.7	59.1	
S3	2.893	1.146	0.8089	6.466	6.4	67.8	
S4	4.142	1.483	1.055	8.196	7.4	60.5	
S5	5.755	2.397	3.075	10.92	9.2	69.2	
S6	5.877	2.407	2.984	10.82	10.6	78.8	
S7	5.84	2.417	3.074	11.12	9.4	76.9	
S8	5.929	2.44	3.058	11.19	9.6	76.7	
S9	6.711	2.593	3.189	11.87	10.8	74.5	
S10	6.695	2.617	3.27	11.9	10.7	86.3	
S11	6.64	2.556	3.254	11.57	10.5	72.2	
S12	8.863	3.398	4.218	17.67	15	87.6	2.6
S13	8.733	3.246	4.061	17.24	14.7	83	3
S14	9.117	3.596	4.459	22.29	18.2	84.9	3.4
S15	9.319	3.661	4.462	22.76	17.7	78.3	3.4
S16	9.858	4.66	4.591	29.03	23.8	83.8	7
S17	9.992	5.225	5.113	33.68	27.3	92.1	7.6
S18	9.828	5.51	4.907	34.81	29.6	85.6	8.4
S19	10.92	7.1	5.053	41.48	37.3	91.9	7.9
S20	23.53	29.82	6.081	161.6	162.7	86.3	49.1
S21	29.95	39.11	6.734	201.5	219	69.5	67.4
S22	109.5	293	65.74	2163	438.7		64.2
S23	841.4	5215	1201	40250	2530.2	29.8	914.3

4.6.1 DWS surface data and 2016 surface data correlation

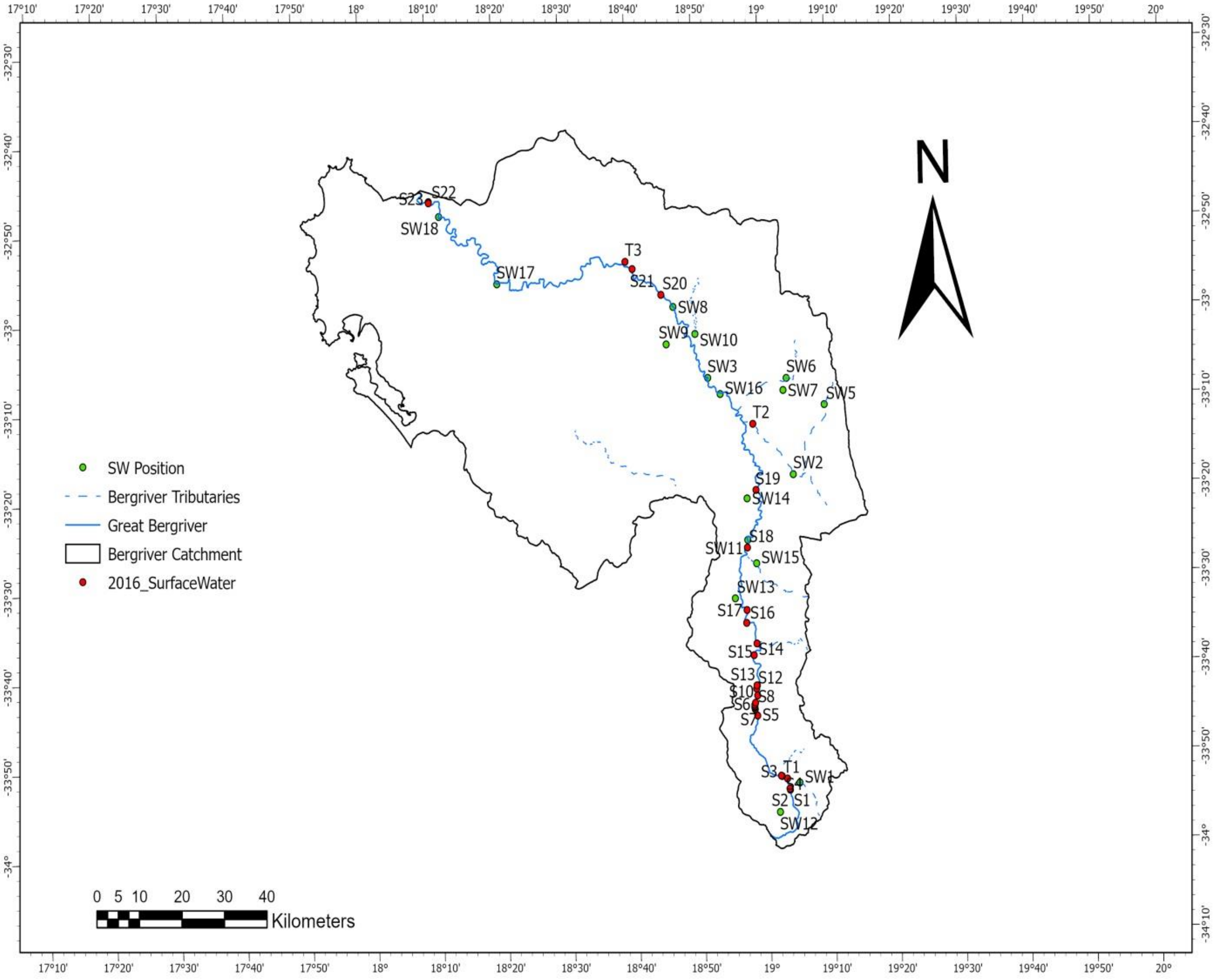

Figure 4.46: DWS Surface Data and 2016 Data sampled by the student

The data from both DWS surface and 2016 surface water sampled by student were grouped according to their geographical locations as explained below:

SW1, SW12, T1 & S1-S3 surface water hydrochemical correlation

The 2016 surface data displayed in Table 4.3 indicated that the 2016 data located in G10A+B quaternary catchment had sown much higher nitrate concentrations compared to the DWS surface data throughout the 11 years studied. The SW1 and SW12 from the DWS had been fairly compliant with drinking water standards set out in SANS 241-1 wherein the SW12 had only exceeded the set limits on two occasions in 11 years whereas SW1 exceeded in 7 out of 11 years. Their nitrates values were much lower compared to the 2016 data for S1, S2, S3 and T1 shown in table 4.3. Their nitrates values ranged between 55.1mg/L and 67.8g/L which far exceed the WHO nitrates limits of 50mg/L for drinking. Thus far it is unclear as to how these values arose to much in a span of 3 years from 2013 where they were below 10mg/L to 2016 where they were above 50mg/L. according to the land-use data displayed in Figure 1.3 and 1.4 of this report, it can be seen that in the entire catchment of BRC the agricultural activities were reduced between 2006-2015 however, urban areas development in the catchment have grown significantly. The urban areas development however, comes with more sewer system challenges which may be a possible explanation to such peculiar rise in nitrates.

SW4, SW13, SW15 and S4-17 surface water hydrochemical correlation

According to the geosoft graphics, it can be distinguished that amongst the samples points in G10C & G10D (SW4, SW13 and SW15), the sample SW13 illustrated values exceeding the drinking water standards set out in SANS 241-1 while SW4 and SW15 only exceeded once in 11 years. These values however were still not close to the 2016 samples which were between 60.5mg/L and 92.1mg/L. Again; there is no possibility of correlating the two as the values are far apart. It is worth noting however that, SW13 and S17 are very close to each other and are adjacent the informal settlement of Mbekweni which had records of continuous sewer overflows from manholes, dilapidated and damaged sewer infrastructure.

Nevertheless, the increase in urban areas development is by far the possible explanation for the abnormal nitrate concentrations. In addition, urban developments for residential habitation result in overloading of municipal sewage system which were already ailing, pipe bursts, overflowing manholes running off in the streets ending up in the river and further by-passing of sewage treatment processes due to ailing infrastructure. The half treated effluent is thus discharged into the river.

S18, S19, SW11 and SW14 surface water hydrochemical correlation

The geosoft graphics indicated that the SW11 and SW14 had moderately high nitrate concentrations. The concentrations however point out to the application of fertilizers since the farms are situated adjacent to the river banks and there are no nearby informal settlements. On the other hand, S18 and S19 recorded higher values similar to other samples from the 2016 surface data wherein S18 had 85.6mg/L nitrates and S19 had 91.9mg/L nitrates concentrations. This however, unlike the samples mentioned above are not situated near major towns or informal settlements, as a result, their sources cannot be pointed to anthropogenic influences but rather agriculture through application of fertilizers. Other parameters were however normal though increasing steadily from S1.

T2, SW3, SW9, SW10 and SW16 surface water hydrochemical correlation

According to the geosoft graphics, the SW3, SW9, SW10 and SW16 were amongst a group of samples which were among the highest records from the DWS data although they were not any close to the 66.6mg/L of nitrates recorded in T2. The area where these samples are located is heavily cultivated and there are no nearby major town and informal settlements with ailing sewer systems. The nitrates are thus as a result of fertilizer application which are easily run-off into the river as the farms are adjacent the river banks.

Furthermore, the DWS samples indicated very high NaCl concentrations of more than 3500mg/L of Cl^- in some years, with SW9 and SW16 taking the lead. In addition, SW9 and SW16 have also recorded concentrations of Na^+ more than 1000mg/L in several years wherein the T2 recorded less NaCl with Na^+ concentration of 103.6mg/L and Cl^- with 94.3mg/L.

S20, S21, T3 and SW8 surface water hydrochemical correlation

Both the DWS surface and the student own data indicates that there are no linkages in this particular area as with rest of the samples in terms of nitrate concentrations. Nonetheless, this area had shown a steep increase in Na^+ and Cl^- wherein S20 recorded Na^+ 161.6mg/L and Cl^- 162.7mg/L and S21 had Na concentration of 201.5mg/L and Cl^- 219mg/L. SW8 however had less than 100mg/L throughout the 11 years studied. T3 however, recorded NaCl concentrations which are fairly low with Na^+ 61.79mg/L and Cl^- 57.8mg/l.

S22, S23, SW17 and SW18 surface water hydrochemical correlation

S22 and S23 recorded significantly high concentrations in all other parameters excluding nitrates. All these samples points however have similarities in high records of all other parameters except nitrates. Their NaCl are particularly high and this may be due to the river water mixing with sea water as the sample location is closer to the sea.

The nitrates in S22 were undetectable whereas the S23 recorded nitrates just below 30mg/L which is significantly low compared to other samples from 2016 data. SW17 and SW18 have also significantly low nitrates throughout the 11 years studied except on two occasions the SW17 had nitrates concentrations just above 1mg/L.

4.7 Summary of results

4.7.1 Surface and groundwater hydrochemical facies correlation

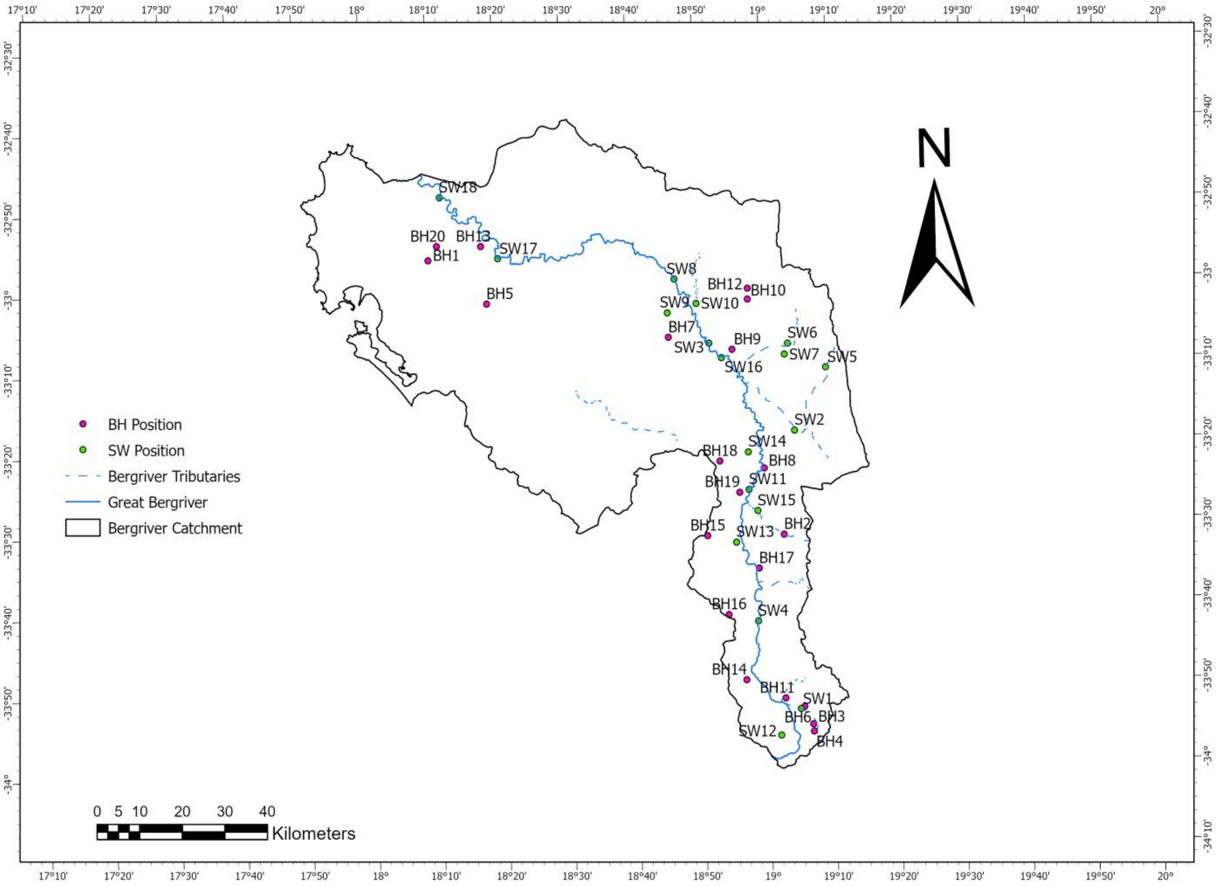

Figure 4.47: DWS Surface and Groundwater locality

The data from both surface and ground water was grouped according to their geographical locations as explained below:

SW1, SW12, BH3, BH4, BH6 and BH11 surface and groundwater hydrochemical correlation

The above sample points are located in the G10A+B quaternary catchment in the BRC headwaters where the lithology is mostly dominated by sandstones of the TMG. The hydrochmeical facies deduce that all the above mentioned samples have the NaCl type. This suggests that the NaCl in the BRC may be originating from the rocks such as siltstone which exists in the upper Berg, although in certain areas it is not dominant however, it is still detectable in the water samples. It can further be observed that surface water samples have both NaCl and Mixed-CaMgCl while groundwater have three additional water types to those of surface including $CaHCO_3$, Mixed $CaNaHCO_3$ and CaCl, it can thus be said there is little to no interaction and transfer of constituents as the water types found in groundwater are not present in surface water.

Furthermore, the Mixed-CaMgCl water type in groundwater is only found in BH3, this further suggest that there may be another factor contributing to the presence of this water type in BH3 as it does not occur in other borehole data.

SW4 and BH14 surface and groundwater hydrochemical correlation

SW4 and BH14 are located in the Paarl area in the G10C quaternary catchment where the underlaying geology is predominant of granitic rocks, most of those belonging to the Cape Granite Suite. Based on the hydrochmeical facies, there is very little movement of water from surface into groundwater, but rather recharge of surface water by groundwater. The borehole in this area records only NaCl water type while surface reflected both NaCl and Mixed-CaMgCl, meaning, this water type does not originate from groundwater but from other factors.

SW13, SW15, BH2, BH15 and BH17 surface and groundwater hydrochemical correlation

Correlation of the above mentioned samples suggest very little interaction of water between the two hydrological components. The groundwater data indicate similarities amongst the boreholes which vary from the surface water. BH2 and BH17 have both NaCl and Mixed-CaMgCl type; however, BH15, SW13 and SW15 have only NaCl water type.

SW11, SW14, BH8, BH18 and BH19 surface and groundwater hydrochemical correlation

The above samples indicate the presence of NaCl and Mixed-CaMgCl water types, therefore it can be said that there is reasonable interaction between the surface and groundwater in this G10F quaternary catchment.

SW8, BH10 and BH12 surface and groundwater hydrochemical correlation

With reference from the hydro-chemical facies, it can be said there is a little interaction and transfer of constituents amongst the above samples. All sample points have NaCl water type, however, BH12 further shown the presence of $CaHCO_3$ water type.

SW17 and BH5 surface and groundwater hydrochemical correlation

The two sample points above are located in the G10L quaternary catchment and both have NaCl water type. It is also worth note-taking that the two sample points are located nearer to the river mouth and therefore, the presence of saline water is inevitable.

SW18, BH1, BH13 and BH20 surface and groundwater hydrochemical correlation

Similar to those of the G10L quaternary catchment, SW18, BH1, BH13 and BH20 are also located in the G10M quaternary catchment, very close to the river mouth into the Atlantic Ocean and as such the dominant NaCl water type is highly inevitable. All the sample points in the G10M indicated no other water type than NaCl.

SW3, SW9, SW10, SW16, BH7 and BH9 surface and groundwater hydrochemical correlation

All the above sample points indicated none other than NaCl water type except for BH3 which reflected both NaCl as well as Mixed-CaMgCl. The presence of Mixed-CaMgCl therefore suggest another factor contributing to its presence as well as no movement of water from surface into groundwater as this water type is not detected in the groundwater.

SW2, SW5, SW6 and SW7 surface and groundwater hydrochemical correlation

The above surface samples could not be correlated with groundwater as there were no available groundwater data in the same vicinity.

4.7.2 Surface and groundwater nitrate correlation

Excessive nitrates are typically found in surface water than in groundwater. Contrary to this notion, in the case of BRC high concentrations of nitrates were found in groundwater compared to surface water. The boreholes that recorded highest nitrates concentrations in most of the years are BH1, BH19, BH20 followed by BH14, BH16 and BH18. Furthermore, higher nitrates concentrations in surface water were found in the sample points SW3, SW9, SW10, SW11, SW13, SW14, and SW16 and occasionally in SW1, SW8 and SW15. Table 4.4 below shows some correlation of excessive surface and groundwater nitrate data.

Table 4. 4: Correlation of excessive SW and GW nitrate data

Quaternary Catchment - Location	**Surface Sample ID**	**Boreholes ID**
G10A - Franschoek	SW1	-
G10C - Paarl	-	BH14 and BH16
G10D - Wellington	SW13 and SW15	-
G10F - Riebeek Kasteel	SW11 and SW14	BH8, BH18 and BH19
G10H - Porterville & Piketberg	SW8	-

G10J - Mooreesburg	SW3, SW9, SW10 and SW16	-
G10M - West Coast	-	BH1 and BH20

The data from both surface and ground water was grouped according to their geographical locations as explained below:

SW1 surface and groundwater nitrates correlation

The SW1 sample had recorded nitrate concentrations that exceed the permissible drinking water standards as stipulated in the SANS 241-1 2015 for more than half the years involved in this research. In most years however, the values were just below 1.2mg/L which is negligible. Only on two occasions the SW1 sample point recorded just above 2mg/L and 8.6mg/L in 2008. This indicates that there may have been accidental discharges or releases of excess nitrates into the river by either malfunctioning Wastewater Treatment Works (WWTW) and or agricultural activities as the area is highly cultivated with various types of grapes and stone fruits. On the other hand however, the report by Cullis et al (2019:156) rules out the possibility of the Franschoek and Wemmershoek being the possible sources of nitrates as they are not listed as part of those which are worst performing in the catchment. The report by DWA (2007) nonetheless indicates that agricultural practices in the area may be the most possible source of excess nitrates by means of fertilizer application and eventually run-off into the river.

Nonetheless, the boreholes (BH3, BH4, BH6 and BH11) in the same area have not recorded nitrates above 1mg/L. although the DWA (2007) report indicated the area of Franshoek and Wemmershoek as one of those highly irrigated in the catchment, the boreholes have very low nitrates. This suggests that the river water used for irrigation may be treated prior to irrigation.

BH14 and BH16 surface and groundwater nitrates correlation

The two boreholes stated above have shown more than 80% of the years recorded higher nitrates concentrations with BH16 taking the lead. The boreholes are located in the vicinity of Paarl which is industrialized, cultivated and also consist of residential areas. The Berg River in the area of Paarl has been recorded to have slightly bad quality of water due to many activities taking place as well as non-compliant WWTW which discharge into the Berg River (DWA, 2007). The possible source of the nitrates however points to agricultural activities by means of irrigation and not fertilizer application as the surface water sample point only recorder 1.7mg/L once in 11 years. The SW4 sample has shown nitrates values less tan 1mg/L in 10 out of 11 years involved in this researched. Another possible explanation to the high nitrates in the boreholes can be pointed to the broken sewage infrastructure (pipes in particular) which may leak into the groundwater system.

SW13 and SW15 surface and groundwater nitrates correlation

SW15 had shown nitrates above 1mg/L only 1 year out 11 years. This suggests an accidental discharge by means of damaged sewage infrastructure. On the hand, SW13 indicated high values of concentrations in 7 out of 11 years. This therefore suggests a constant feeder of nitrates into the river such as an ailing sewage system and damaged sewage infrastructure. SW13 is situated adjacent the area of Mbekweni between Paarl and Wellington. Mbekweni is an informal settlement and has an ailing wastewater infrastructure like most informal settlements in the country. The sewage run-off (overflowing manholes) directly into the Berg River as it passes adjacent to the informal settlement. Although SW13 and SW15 are in the same quaternary catchment but recorded highly variable nitrates suggest a significant dilution and or the presence of marine organisms which consumes the parameter at hand. Furthermore, the boreholes (BH2, BH15 and BH17) have shown the record of very low nitrate concentrations contrary to surface data. This may be due to the fact that there are no agricultural activities in the vicinity and further there may be significantly low or no interchange of surface and groundwater.

SW11, SW14, BH8, BH18 and BH19 surface and groundwater nitrates correlation

The sample points stated above had shown moderately high nitrate concentrations. The area of Riebeek Katseel is also highly cultivated and irrigation with river water is highly practiced. The possible source of nitrates in surface water can be pointed to the application of fertilizers which is transported to the Berg River by run-off. It is also worth note taking that the farms in this area are adjacent to the Berg River; as a result, fertilizers are easily transported into the river. In addition, the boreholes in the area have also shown significant concentrations of nitrates with BH18 going up to 16.8mg/L of nitrates. This notion therefore points suggest that there is irrigation with the untreated river water and insignificant dilution in groundwater compared to surface water.

SW8 surface and groundwater nitrates correlation

This sample point only recorded on one occasion values exceeding 1mg/L of nitrates. This may have been due to an accidental discharge of sewage.

SW3, SW9, SW10 and SW16 surface and groundwater nitrates correlation

SW3 has recorded values exceeding the permissible limits only in 2 out of 11 years and SW9 in 3 out of 11 years. Such inconsistencies point to accidental discharges such as overflowing manholes. SW10 and SW16 on the other hand have moderately high nitrate concentrations compared to SW3 and SW9. All the surface samples stated above are situated in the area of Mooreesburg which is highly cultivated. Therefore, application of fertilizers is the most possible source of excessive nitrates in the River in the vicinity. In addition, the area is dominated by farm houses and a small informal settlement of the farm workers such as Gouda. Most of the farm houses use septic tanks whereas areas like Gouda use the Oxidation Ponds as their sewage system and discharge directly into the Berg River. The sewage discharge from the Gouda Oxidation Ponds however, cannot be pointed as the leading source of excessive nitrates in the River as it has not been listed as one of the worst performing (Cullis et al., 2019:155-159).

There is however no corresponding groundwater data which have recorded abnormal nitrates concentrations in the vicinity. BH7 and BH9 in the vicinity of Mooreesburg have indicated significantly low nitrates throughout 11 years. This further indicates little or no interchange of surface and groundwater as there is no evidence of exchange of constituents. In addition, the low nitrates in the boreholes data may also suggest that irrigation is practiced with treated river water.

BH1 and BH20 surface and groundwater nitrates correlation

BH1 and BH20 are located in the West Coast known for the cultivation of stone fruits and winter cereals. These two boreholes recorded the highest nitrate concentrations amongst all other boreholes with BH20 recording high values all throughout the 11 years, with the 2008 being the highest with the record of 22.11mg/L. on the contrary, the surface water samples in the area, SW17 and SW18 have shown incredibly low nitrate concentrations all throughout 11 years.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Water is a precious and yet a scarce resource which is extremely crucial for the life on Earth. In South Africa, water is crucial not only for the socio-economic development but for other forms of ecosystems at large. As a result, it is therefore important to investigate, to monitor, to record, to rectify water quality degradation and to hold accountable those who degrade the water resources. The above statement is supported by the Constitution of South Africa delineated in Section 24 which stated as follows: “Section 24 (b) states that “everyone has the right to have the environment protected for the benefit of present and future generations, through reasonable legislative and other measures”. The Constitution therefore gave powers to other environmental legal frameworks such as the National Water Act 36 of 1998 which in its Section 2 states that “the Act aims to protect, use, develop, conserve, manage and control water resources as a whole, promoting the integrated management of water resources with the participation of all stakeholders”.

Therefore, this study was investigating the hydrogeochemical interactions between surface and groundwater in the BRC with the aim of establishing trends and transfer of constituents between the surface and groundwater systems. The hydrochemical facies indicated that in the upper Berg River Catchment, there is very minimal interaction between surface and groundwater systems. Other water types that were found in the groundwater either than NaCl were barely found in surface water and vice versa. This may be due to the underlying consolidated hard rock formations (granitic rocks) having less geohydrological properties like fractures and voids.

The Middle Berg however, indicated a degree of interaction with sharing of constituents between the two water systems. Most of the water types found in borehole data were also found in the surface water. This can be explained with reference to the structural geology of the area in which a northwest-trending strike-slip faults of the Piketberg-Wellington faults occurred which gave rise to more permeability and movement of water.

Moreover, the Lower Berg indicated only NaCl water type. It is worth note taking that the Lower Berg is situated near the river mouth whereby there is mixing of river and sea water. This notion therefore further explains the NaCl being the sole water type in the area. In surface water this may have further been exacerbated by means of sea spray. With reference to groundwater, Clark & Ractliffe, (2007) highlighted that there may have been a possibility of sea water intrusion also enhanced by the faulting of rocks originated from the Colenso fault.

With reference to nitrates, the data indicated no interaction and transfer of constituents. Table 4.4 in Chapter 4 illustrate that there are 3 boreholes (BH8, BH18 and BH19) which were correlated with the 2 surface samples (SW11 and SW14). The rest of the surface and groundwater samples did not indicate correspondence. It can therefore be deduced that the nitrates in the boreholes came by as a result of using nitrate rich water from agricultural activities like irrigation.

Overall, the results obtained in this study indicated that:

i) The entire catchment geology consist of rocks containing various minerals with varying chemical make-up however, the NaCl exist in the entire geology even though in some areas it is not dominant,

ii) the geology and soils do not entirely control the water chemistry of the surface water however, in areas which have been affected by geological faults, there were correlation of water chemistry between the surface and groundwater systems,

iii) The surface and groundwater interaction and transfer of constituents occurs mostly in the Middle Berg, and

iv) Nitrates in the boreholes are believed to be a result of agricultural activities like irrigation with nitrate rich water.

5.1 Recommendations

- Careful monitoring of the water quality used to irrigate must be conducted by the Department of Water and Sanitation and the Berg River Catchment Irrigation Board to ensure that farmers who conduct irrigation comply with the irrigation standards to avoid contamination of groundwater through this process.
- A considerable need to better improve the monitoring system for potential point and non-point sources with reference to nitrates and salinity in both surface and

groundwater systems in the BRC. One of the ways to achieve this is through conduction of another study using the stable isotopes.

- Enforcement by the DWS as the regulating authority of all water resources in the country must be strengthened.
- Cooperative Governance between the DWS as well the Municipalities in the BRC must further be strengthened.

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APPENDICES

APPENDIX A: DATA FROM NATIONAL WATER MONITORING DATABASE

2003 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	7.270776	2.708612	16.75039	3.31851	5.780235	22.72414	25.07604	11.1821	1.127224
SW2	-33.31389	19.07472	5.069235	4.340353	17.42544	1.661824	5.080806	19.97444	31.89918	8.426559	0.2815
SW3	-33.13083	18.86278	5.412805	3.083463	17.18295	2.023951	4.911398	19.30844	27.69985	9.127537	0.739146
SW4	-33.7075	18.97444	4.576439	2.166098	8.832268	1.647829	2.881866	11.32963	15.94271	7.569976	0.63922
SW5	-33.18472	19.15528	2.2545	1.40975	3.877625	0.247875	2.61866	10.29488	5	2.969	0.092125
SW6	-33.13389	19.06083	1.4	1.225	3.775	0.15	1.98405	7.8	4.875	4.2	0.03094
SW7	-33.15667	19.05222	0.921	0.5	5.000333	0.15	1.199587	4.716	5	2	0.044791
SW8	-32.99694	18.77889	6.804293	4.581976	25.34376	2.222171	5.625805	22.11702	44.35668	12.85476	0.566366
SW9	-33.06611	18.75972	181.3572	245.3759	1970.338	38.72931	82.80647	325.5414	3584.261	408.9009	0.217313
SW10	-33.04778	18.83278	48.73215	71.34825	359.3371	12.36675	28.74723	113.0155	703.1922	136.9651	0.8509
SW11	-33.435	18.95694	6.133136	2.815068	18.9365	2.934295	5.524284	21.71791	26.01045	10.20223	1.572614
SW12	-33.94417	19.0275	1.060893	0.865536	2.797036	0.202643	0.902952	3.549821	5	4.748929	1.028
SW13	-33.54333	18.9225	48.76133	47.7815	349.5623	8.013833	43.92211	172.6733	588.8457	108.5537	0.755083
SW14	-33.35722	18.95694	33.82142	44.08275	222.261	6.673167	26.64337	104.7445	416.4878	74.35267	0.457083
SW15	-33.47917	18.97806	5.98536	3.40032	17.20848	1.32512	5.669631	22.28932	28.39584	11.3446	0.37156
SW16	-33.16139	18.89306	185.6444	287.3728	1659.339	25.2252	33.27369	130.8106	3265.245	586.8816	0.2726
SW17	-32.94583	18.33667	20.178	21.25	127.658	4.598	13.22395	51.988	229.985	39.844	0.055
SW18	-32.81667	18.19417	364.034	931.804	7731.638	304.106	36.14455	142.097	14598.22	1816.259	0.055

2004 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	7.61676	3.10652	15.0047	3.09254	6.011264	23.6324	25.1055	10.08384	0.84074
SW2	-33.31389	19.07472	4.782571	4.815238	18.18886	1.664857	4.476007	17.59676	34.00257	10.81367	0.334905
SW3	-33.13083	18.86278	6.87145	5.0054	26.19155	2.6184	5.600795	22.0187	45.95905	15.26285	0.64835
SW4	-33.7075	18.97444	4.776261	2.418261	9.242261	2.082435	3.077179	12.09748	17.3033	8.745043	0.698304
SW5	-33.18472	19.15528	1.3526	0.9976	3.7238	0.2894	1.59833	6.2836	5	5.6288	0.12
SW6	-33.13389	19.06083	1.1	0.5	2.5	0.38	0.508731	2	5.1	2	0.028265
SW7	-33.15667	19.05222	0.85	0.5	4.0525	0.4615	0.508731	2	5.85	6.107	0.0326
SW8	-32.99694	18.77889	8.388105	7.186526	39.59121	2.633895	6.363739	25.01811	71.01089	20.18837	0.648158
SW9	-33.06611	18.75972	227.2719	248.5952	1607.843	55.81613	87.60043	344.3882	3187.617	355.1024	0.598125
SW10	-33.04778	18.83278	62.93315	88.33023	437.9615	11.72892	31.59108	124.1957	915.7166	156.9134	1.023615
SW11	-33.435	18.95694	6.81435	3.6446	22.47945	3.08295	6.080896	23.90615	35.2562	13.91825	0.9377
SW12	-33.94417	19.0275	1.30114	0.63244	2.85488	0.21018	1.043539	4.10252	5.19178	6.17354	0.04822
SW13	-33.54333	18.9225	147.7659	119.3232	720.9094	19.36811	77.27603	303.7993	1372.158	229.2663	3.233
SW14	-33.35722	18.95694	41.10044	41.02678	224.5304	8.212556	26.56753	104.4463	419.2144	83.84189	1.424222
SW15	-33.47917	18.97806	17.92406	5.924875	28.01713	1.36225	5.825937	22.90381	45.41294	37.06906	3.522688
SW16	-33.16139	18.89306	156.9349	161.6749	1078.221	22.63467	60.75974	238.868	2030.655	312.836	4.06
SW17	-32.94583	18.33667	19.676	23.89	152.06	6.422	16.19748	63.678	269.209	51.027	0.055
SW18	-32.81667	18.19417	297.783	975.484	7438.54	302.318	37.03153	145.584	11816.2	1695.865	0.155

2005 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	7.8808	2.6214	10.9598	2.4098	5.664462	22.269	20.4724	11.1966	0.995
SW2	-33.31389	19.07472	5.703043	6.379043	23.15135	2.156435	6.444955	25.33739	44.75774	12.6583	0.04
SW3	-33.13083	18.86278	6.595727	4.549864	21.59132	2.369682	5.511993	21.66959	41.75268	13.98371	3.511
SW4	-33.7075	18.97444	4.329143	2.345857	7.914	1.96	2.548305	10.01829	17.31443	7.105429	1.758
SW5	-33.18472	19.15528	1.0548	0.5	2.7316	0.3054	1.361363	5.352	5	5.5694	0.05
SW6	-33.13389	19.06083	2.635	0.5	3.62	0.4005	2.001983	7.8705	5	5.273	0.893
SW7	-33.15667	19.05222	1.1705	0.5725	4.42025	0.287	1.208776	4.752125	5.6795	4.778	2.334
SW8	-32.99694	18.77889	8.802348	7.349478	37.25422	2.725304	6.585619	25.89039	70.20965	17.32204	0.03
SW9	-33.06611	18.75972	150.8635	237.6648	1626.054	33.82705	86.98783	341.9798	3122.797	306.6595	0.54
SW10	-33.04778	18.83278	44.2286	74.5875	330.5014	8.7062	33.79129	132.8455	654.471	121.2695	0.285
SW11	-33.435	18.95694	6.989214	3.766357	19.3925	2.9265	5.375013	21.13107	32.7855	13.10779	0.098
SW12	-33.94417	19.0275	1.327313	0.64525	2.731625	0.213	1.133134	4.45475	5.500063	4.757313	2.13
SW13	-33.54333	18.9225	79.328	90.46013	520.5101	13.90013	59.61338	234.3613	967.4201	158.9385	1.558
SW14	-33.35722	18.95694	32.991	38.34229	196.7614	6.853571	21.64696	85.10186	349.7999	75.635	1.657
SW15	-33.47917	18.97806	14.23417	6.560667	39.11592	1.829	7.982409	31.38167	63.258	32.8975	0.21
SW16	-33.16139	18.89306	153.9905	223.2328	1353.084	18.56517	67.56008	265.6025	2654.41	411.1715	0.5
SW17	-32.94583	18.33667	7.908	6.209	33.224	4.096	6.361423	25.009	60.44	14.827	0.317
SW18	-32.81667	18.19417	418.476	1021.945	8956.527	338.855	33.25089	130.721	16425.39	2521.484	0.102

2006 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	10.59925	2.66725	20.4355	5.7405	10.15331	39.91625	31.44475	8.40325	1.28475
SW2	-33.31389	19.07472	5.444833	5.700292	22.60583	1.826458	6.065024	23.84375	42.29688	7.222625	0.077625
SW3	-33.13083	18.86278	6.032273	3.647	21.06564	2.617364	5.290996	20.80077	33.82023	8.957818	0.618818
SW4	-33.7075	18.97444	4.798875	1.906208	8.429208	1.970333	2.906336	11.42583	17.40671	5.872583	0.533292
SW5	-33.18472	19.15528	2.09525	1.23775	3.44325	0.255	2.531317	9.9515	5.84675	3.3665	0.06625
SW6	-33.13389	19.06083	1.614	0.5	2.833	0.394	1.017461	4	2	2	0.03575
SW7	-33.15667	19.05222	1.247833	0.796667	3.623167	0.184833	1.197722	4.708667	5	4.951	0.1015
SW8	-32.99694	18.77889	7.493185	5.129259	26.37185	2.566222	6.237858	24.52322	46.60526	11.80141	0.270519
SW9	-33.06611	18.75972	204.8038	290.0701	2047.688	35.32381	128.5435	505.35	3852.065	354.9017	0.058313
SW10	-33.04778	18.83278	51.5835	86.1308	430.9565	8.7543	36.58939	143.8458	783.4553	143.2312	0.3949
SW11	-33.435	18.95694	6.28632	2.72876	18.7554	3.2836	5.855867	23.02148	27.05292	9.44496	1.30416
SW12	-33.94417	19.0275	1.079	0.595	2.183167	0.187	1.183901	4.654333	5.922833	3.918667	0.038833
SW13	-33.54333	18.9225	42.89	46.45643	266.4611	5.577429	32.76106	128.7953	467.0901	83.38986	1.382571
SW14	-33.35722	18.95694	32.8525	39.568	202.393	4.692	23.02261	90.51	353.5805	66.9905	2.4605
SW15	-33.47917	18.97806	7.33325	2.621875	12.92738	1.0425	5.18616	20.38863	20.26875	15.97443	0.099625
SW16	-33.16139	18.89306	186.3963	323.0857	1379.99	12.871	88.07604	346.258	2843.626	357.6577	0.031667
SW17	-32.94583	18.33667	18.452	21.429	147.317	4.27	9.760762	38.373	273.224	38.753	0.04
SW18	-32.81667	18.19417	318.643	857.781	7097.504	265.445	28.67435	112.729	12887.41	1975.515	0.133

2007 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	11.45	3.065684	19.41421	4.450316	7.080969	27.83779	30.67842	10.17695	2.138737
SW2	-33.31389	19.07472	5.084269	5.281923	20.71477	1.706308	5.445238	21.40715	39.82085	6.955231	0.071231
SW3	-33.13083	18.86278	5.762192	3.632308	18.95942	2.26	5.341946	21.00108	32.06235	8.768115	0.339115
SW4	-33.7075	18.97444	5.14128	2.36132	10.17972	2.12712	3.092594	12.15808	18.72172	8.04192	0.67512
SW5	-33.18472	19.15528	1.542333	1.0005	4.583333	0.340667	2.320278	9.121833	7.278667	3.575167	0.055
SW6	-33.13389	19.06083	0.92525	1.06475	3.426	0.2845	1.017461	4	7.10575	3.05625	0.02
SW7	-33.15667	19.05222	1.3815	0.856	5.036	0.284	1.708826	6.718	11.0485	2	0.059
SW8	-32.99694	18.77889	7.793615	5.376038	27.93804	2.840077	6.532044	25.67977	48.46915	11.59562	0.274346
SW9	-33.06611	18.75972	167.4108	277.9128	1978.638	37.53258	97.27346	382.4163	3662.494	333.3878	0.051053
SW10	-33.04778	18.83278	34.99025	57.209	277.664	8.05525	30.49116	119.8715	507.7065	96.1195	0.31025
SW11	-33.435	18.95694	6.591077	3.176346	21.28231	3.564077	6.942589	27.29377	29.34208	10.66723	0.718885
SW12	-33.94417	19.0275	0.8655	0.5	3.082	0.307	1.017461	4	6.8735	3	0.055
SW13	-33.54333	18.9225	72.25429	83.01386	461.6796	11.19943	60.98246	239.7436	836.021	145.9873	0.307
SW14	-33.35722	18.95694	32.12267	39.742	217.953	5.087333	29.3853	115.524	357.6823	81.81633	1.902333
SW15	-33.47917	18.97806	3.975267	2.544867	10.1566	0.666133	3.260269	12.81727	17.32133	8.526667	0.088533
SW16	-33.16139	18.89306	254.519	504.9608	2038.596	21.09225	42.39857	166.6838	4471.288	566.9013	0.0685
SW17	-32.94583	18.33667	13.815	20.16	133.853	4.746	11.49477	45.19	234.918	37.201	1.909
SW18	-32.81667	18.19417	251.701	624.239	5312.068	201.998	28.77483	113.124	9545.52	1251.781	0.04

2008 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	23.27267	4.354	47.26333	11.03567	15.78312	62.049	63.87367	18.15767	8.660667
SW2	-33.31389	19.07472	4.33116	4.36284	16.43532	1.936	3.693772	14.52152	31.48016	7.15732	0.19508
SW3	-33.13083	18.86278	7.5962	4.287	21.52724	2.89916	5.845723	22.9816	37.30052	9.8808	0.79356
SW4	-33.7075	18.97444	5.036167	2.375042	9.028167	2.177042	2.902309	11.41	17.65775	6.324458	0.672667
SW5	-33.18472	19.15528	1.760556	0.843556	3.629111	0.204333	2.254921	8.864889	6.503222	3.999333	0.068444
SW6	-33.13389	19.06083	0.8194	0.4	3.0626	0.1894	1.049206	4.1248	5.095	3.3674	0.0405
SW7	-33.15667	19.05222	1.64	0.9272	4.192	0.3848	1.017461	4	9.539	2.4158	0.034833
SW8	-32.99694	18.77889	8.96348	6.50336	30.23188	3.08544	6.622758	26.0364	57.47216	13.18196	0.57728
SW9	-33.06611	18.75972	187.3481	275.5728	1898.503	39.42871	93.85051	368.9595	3598.953	341.7656	0.161412
SW10	-33.04778	18.83278	40.00843	62.357	329.9239	11.04386	27.351	107.5264	588.9954	119.0281	1.329286
SW11	-33.435	18.95694	7.46688	3.39332	18.24184	3.26068	5.560274	21.8594	28.65592	10.12184	1.12544
SW12	-33.94417	19.0275	2.478	0.25	2.899	0.425	2.745365	10.793	4.688	1.45	0.212
SW13	-33.54333	18.9225	62.02571	66.37686	375.2216	10.43979	46.14035	181.394	686.8918	110.7617	1.302714
SW14	-33.35722	18.95694	34.1288	42.66	208.8552	8.4421	31.29564	123.0342	362.9631	78.7679	1.6139
SW15	-33.47917	18.97806	5.3635	3.625357	16.30629	1.245286	3.838119	15.089	28.79929	12.17271	0.2685
SW16	-33.16139	18.89306	127.7363	213.258	1197.804	22.29167	34.99881	137.5927	2349.772	341.272	0.04
SW17	-32.94583	18.33667	26.241	29.541	183.323	8.01	14.2437	55.997	352.739	56.467	0.04
SW18	-32.81667	18.19417	63.025	152.012	1254.7	53.84	17.38765	68.357	1194.011	307.059	0.012

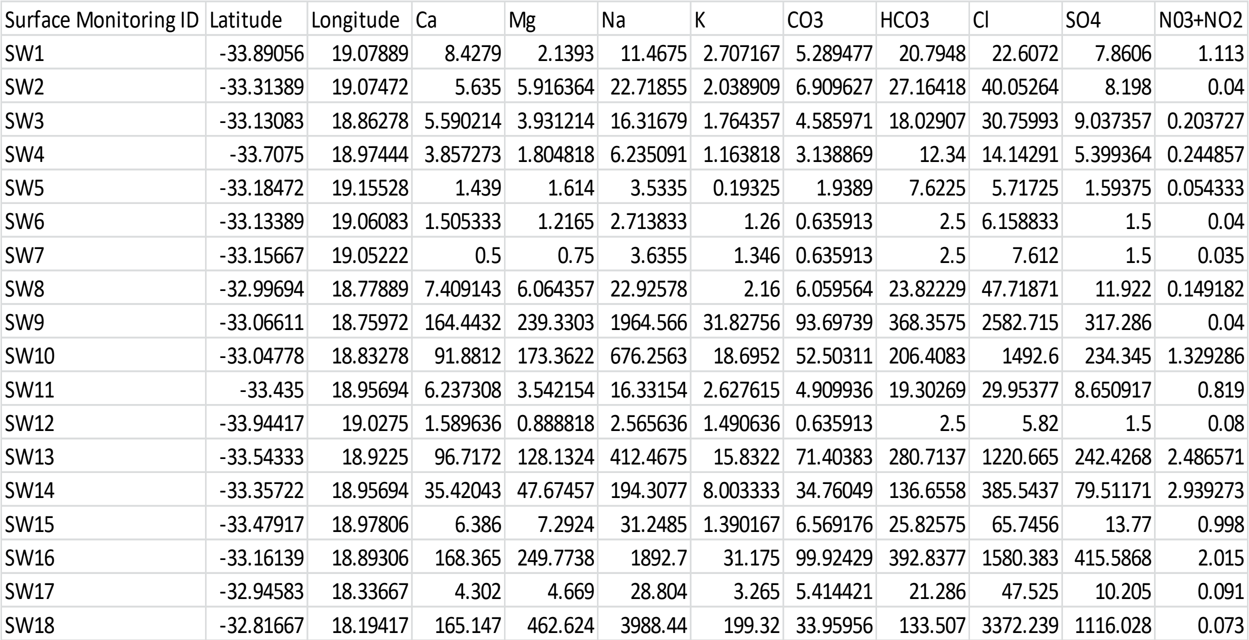
2009 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	9.859	3.208667	13.9925	2.645333	7.373289	28.987	22.20367	11.17867	0.6865
SW2	-33.31389	19.07472	4.951529	5.558765	18.22876	1.494059	4.723804	18.57094	35.53747	10.26306	0.361294
SW3	-33.13083	18.86278	7.8725	6.007731	30.34631	2.744077	5.799745	22.80085	56.36581	14.09015	0.822308
SW4	-33.7075	18.97444	5.098346	2.479962	9.155077	2.0805	3.468418	13.63558	17.14292	9.273962	0.732077
SW5	-33.18472	19.15528	1.8688	0.9188	3.6443	0.2483	2.262071	8.893	6.2141	2.493	0.0558
SW6	-33.13389	19.06083	1.5592	0.75	3.576	1.5018	0.92238	3.6262	7.08	1.05	0.04
SW7	-33.15667	19.05222	1.11275	1.23375	3.519333	1.2345	5.179333	5.179333	9.17125	1.5	0.028
SW8	-32.99694	18.77889	10.40596	9.53244	47.92308	2.99992	7.173174	28.20028	89.09552	19.26428	0.78664
SW9	-33.06611	18.75972	167.4593	235.5328	1390.517	29.77813	83.52082	328.3498	2664.793	322.1159	0.276067
SW10	-33.04778	18.83278	60.00525	106.0441	513.3386	12.15275	40.46702	159.0901	954.6956	167.272	1.290625
SW11	-33.435	18.95694	7.188769	3.695731	18.45696	2.966077	4.891524	19.23031	32.59654	10.66438	1.237154
SW12	-33.94417	19.0275	1.240667	0.5	2.732333	0.293333	1.017461	4	4.657333	2	0.212
SW13	-33.54333	18.9225	79.28336	102.4884	585.3846	14.72364	67.54034	265.5249	1055.072	176.9356	1.284182
SW14	-33.35722	18.95694	48.204	74.11773	356.6075	7.702091	41.32947	162.4807	630.1185	118.1155	2.939273
SW15	-33.47917	18.97806	5.890222	5.220833	21.85833	1.427444	5.309439	20.87328	39.18094	15.08033	0.275944
SW16	-33.16139	18.89306	198.1489	307.6228	1847.653	28.86833	72.56785	285.2898	3533.808	541.575	0.95825
SW17	-32.94583	18.33667	10.312	17.469	63.629	3.642	9.725405	38.234	123.071	19.056	0.196
SW18	-32.81667	18.19417	36.186	67.777	549.645	27.014	15.91335	62.561	1110.361	143.156	0.025

2010 Surface Data

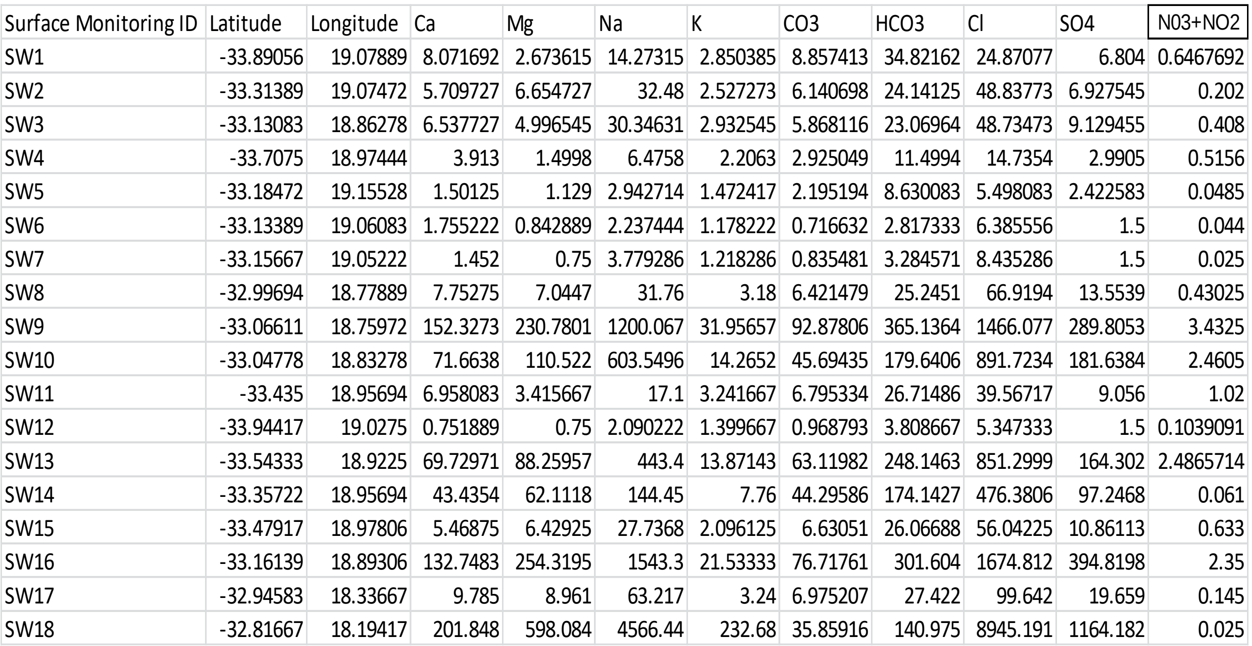
Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	9.220667	3.124	13.20067	2.676333	4.919087	19.33867	23.14367	10.83733	1.403667
SW2	-33.31389	19.07472	5.34576	5.64408	18.63736	1.83628	4.790351	18.83256	35.40884	9.5384	0.3414
SW3	-33.13083	18.86278	8.165583	6.57975	33.19258	2.758583	6.066465	23.84942	57.77196	14.68625	0.673792
SW4	-33.7075	18.97444	5.18	2.330885	10.03808	2.261192	3.157437	12.413	17.59977	8.083462	0.629615
SW5	-33.18472	19.15528	1.749	1.22625	3.933	0.201625	2.26754	8.9145	6.40475	2.405875	0.069125
SW6	-33.13389	19.06083	1.8595	0.75	2.746	0.665	0.635913	2.5	5.2625	1.5	0.06075
SW7	-33.15667	19.05222	1.7	1.775	3.3275	0.4835	0.635913	2.5	9.333	2.55	0.0655
SW8	-32.99694	18.77889	10.13177	9.916038	48.64954	3.032115	7.728686	30.38419	87.37027	18.17304	0.539885
SW9	-33.06611	18.75972	149.6348	197.0848	1273.304	26.65753	90.22902	354.7221	2392.415	299.3491	1.268412
SW10	-33.04778	18.83278	68.63857	100.2339	488.492	13.80871	38.47825	151.2716	936.7756	171.3289	2.232571
SW11	-33.435	18.95694	8.41892	4.61856	24.92576	3.49796	6.386178	25.10632	40.58724	12.59448	1.16168
SW12	-33.94417	19.0275	0.617667	0.75	0.59575	0.90775	0.998045	3.923667	5.845333	1.456	0.093667
SW13	-33.54333	18.9225	118.5958	134.3846	735.9397	19.85533	81.92144	322.0621	1363.853	235.2832	3.0535
SW14	-33.35722	18.95694	45.3633	59.2322	278.3484	8.182	39.85814	156.6964	515.5952	89.0346	1.2752
SW15	-33.47917	18.97806	6.624	6.407556	30.30311	1.450056	6.131095	24.1035	52.66283	16.63772	0.334056
SW16	-33.16139	18.89306	124.4569	193.8566	1214.965	19.47356	77.27868	303.8098	1958.586	333.9942	1.610778
SW17	-32.94583	18.33667	12.012	15.914	64.945	2.574	9.325034	36.66	134.852	19.603	0.25
SW18	-32.81667	18.19417	207.817	720.275	5081.36	210.76	35.29472	138.756	1501.973	996.663	0.25

2011 Surface Data



Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	8.4279	2.1393	11.4675	2.707167	5.289477	20.7948	22.6072	7.8606	1.113
SW2	-33.31389	19.07472	5.635	5.916364	22.71855	2.038909	6.909627	27.16418	40.05264	8.198	0.04
SW3	-33.13083	18.86278	5.590214	3.931214	16.31679	1.764357	4.585971	18.02907	30.75993	9.037357	0.203727
SW4	-33.7075	18.97444	3.857273	1.804818	6.235091	1.163818	3.138869	12.34	14.14291	5.399364	0.244857
SW5	-33.18472	19.15528	1.439	1.614	3.5335	0.19325	1.9389	7.6225	5.71725	1.59375	0.054333
SW6	-33.13389	19.06083	1.505333	1.2165	2.713833	1.26	0.635913	2.5	6.158833	1.5	0.04
SW7	-33.15667	19.05222	0.5	0.75	3.6355	1.346	0.635913	2.5	7.612	1.5	0.035
SW8	-32.99694	18.77889	7.409143	6.064357	22.92578	2.16	6.059564	23.82229	47.71871	11.922	0.149182
SW9	-33.06611	18.75972	164.4432	239.3303	1964.566	31.82756	93.69739	368.3575	2582.715	317.286	0.04
SW10	-33.04778	18.83278	91.8812	173.3622	676.2563	18.6952	52.50311	206.4083	1492.6	234.345	1.329286
SW11	-33.435	18.95694	6.237308	3.542154	16.33154	2.627615	4.909936	19.30269	29.95377	8.650917	0.819
SW12	-33.94417	19.0275	1.589636	0.888818	2.565636	1.490636	0.635913	2.5	5.82	1.5	0.08
SW13	-33.54333	18.9225	96.7172	128.1324	412.4675	15.8322	71.40383	280.7137	1220.665	242.4268	2.486571
SW14	-33.35722	18.95694	35.42043	47.67457	194.3077	8.003333	34.76049	136.6558	385.5437	79.51171	2.939273
SW15	-33.47917	18.97806	6.386	7.2924	31.2485	1.390167	6.569176	25.82575	65.7456	13.77	0.998
SW16	-33.16139	18.89306	168.365	249.7738	1892.7	31.175	99.92429	392.8377	1580.383	415.5868	2.015
SW17	-32.94583	18.33667	4.302	4.669	28.804	3.265	5.414421	21.286	47.525	10.205	0.091
SW18	-32.81667	18.19417	165.147	462.624	3988.44	199.32	33.95956	133.507	3372.239	1116.028	0.073

2012 Surface Data



Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	8.071692	2.673615	14.27315	2.850385	8.857413	34.82162	24.87077	6.804	0.6467692
SW2	-33.31389	19.07472	5.709727	6.654727	32.48	2.527273	6.140698	24.14125	48.83773	6.927545	0.202
SW3	-33.13083	18.86278	6.537727	4.996545	30.34631	2.932545	5.868116	23.06964	48.73473	9.129455	0.408
SW4	-33.7075	18.97444	3.913	1.4998	6.4758	2.2063	2.925049	11.4994	14.7354	2.9905	0.5156
SW5	-33.18472	19.15528	1.50125	1.129	2.942714	1.472417	2.195194	8.630083	5.498083	2.422583	0.0485
SW6	-33.13389	19.06083	1.755222	0.842889	2.237444	1.178222	0.716632	2.817333	6.385556	1.5	0.044
SW7	-33.15667	19.05222	1.452	0.75	3.779286	1.218286	0.835481	3.284571	8.435286	1.5	0.025
SW8	-32.99694	18.77889	7.75275	7.0447	31.76	3.18	6.421479	25.2451	66.9194	13.5539	0.43025
SW9	-33.06611	18.75972	152.3273	230.7801	1200.067	31.95657	92.87806	365.1364	1466.077	289.8053	3.4325
SW10	-33.04778	18.83278	71.6638	110.522	603.5496	14.2652	45.69435	179.6406	891.7234	181.6384	2.4605
SW11	-33.435	18.95694	6.958083	3.415667	17.1	3.241667	6.795334	26.71486	39.56717	9.056	1.02
SW12	-33.94417	19.0275	0.751889	0.75	2.090222	1.399667	0.968793	3.808667	5.347333	1.5	0.1039091
SW13	-33.54333	18.9225	69.72971	88.25957	443.4	13.87143	63.11982	248.1463	851.2999	164.302	2.4865714
SW14	-33.35722	18.95694	43.4354	62.1118	144.45	7.76	44.29586	174.1427	476.3806	97.2468	0.061
SW15	-33.47917	18.97806	5.46875	6.42925	27.7368	2.096125	6.63051	26.06688	56.04225	10.86113	0.633
SW16	-33.16139	18.89306	132.7483	254.3195	1543.3	21.53333	76.71761	301.604	1674.812	394.8198	2.35
SW17	-32.94583	18.33667	9.785	8.961	63.217	3.24	6.975207	27.422	99.642	19.659	0.145
SW18	-32.81667	18.19417	201.848	598.084	4566.44	232.68	35.85916	140.975	8945.191	1164.182	0.025

2013 Surface Data

Surface Monitoring ID	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	N03+NO2
SW1	-33.89056	19.07889	10.38923	2.228077	21.68262	4.927462	10.58609	41.61764	34.063	10.53777	5.155
SW2	-33.31389	19.07472	5.051	4.8475	19.65611	2.1302	5.467863	21.4961	37.9946	5.8538	0.427
SW3	-33.13083	18.86278	6.675889	4.760778	25.91611	2.989444	5.691142	22.37389	50.473	9.997778	1.06625
SW4	-33.7075	18.97444	4.0556	1.4638	7.5122	2.271	3.055131	12.0108	15.4052	3.2953	0.6265
SW5	-33.18472	19.15528	1.552667	1.297778	2.595222	1.378889	2.000075	7.863	5.042	2.833333	0.0503333
SW6	-33.13389	19.06083	1.91975	0.75	3.419833	1.205083	1.101381	4.329917	6.174833	1.5	0.025
SW7	-33.15667	19.05222	2.236667	0.75	4.1235	1	1.342795	5.279	9.417667	1.5	0.112
SW8	-32.99694	18.77889	9.0069	8.636833	47.645	3.5338	8.436663	33.1675	87.7564	17.0309	1.288
SW9	-33.06611	18.75972	148.0011	240.9173	1305.358	29.94629	93.13826	366.1594	1261.131	283.9176	1.6645
SW10	-33.04778	18.83278	57.7284	115.5578	484.8396	10.9618	41.14329	161.7488	1156.933	148.6188	3.1732
SW11	-33.435	18.95694	5.814455	3.019636	18.28255	2.967455	4.670795	18.36255	32.36345	7.986182	1.3036364
SW12	-33.94417	19.0275	52.8802	62.9266	508.602	10.0227	48.13605	189.2398	680.2117	110.75	0.0352222
SW13	-33.54333	18.9225	52.8802	62.9266	508.602	10.0227	48.13605	189.2398	680.2117	110.75	1.7631667
SW14	-33.35722	18.95694	41.7155	55.12475	217.7943	8.879	38.75301	152.3518	404.4198	71.8075	0.1075
SW15	-33.47917	18.97806	3.848375	4.279	22.12775	1.790875	4.829222	18.98538	39.44588	7.28925	0.08975
SW16	-33.16139	18.89306	120.129	225.9016	1122.607	21.5674	82.73971	325.279	1380.751	382.7106	1.3584
SW17	-32.94583	18.33667	19.359	25.353	185.71	8.34	12.17647	47.87	312.742	57.39	0.025
SW18	-32.81667	18.19417	18.391	24.049	179.673	8.01	11.88751	46.734	300.888	47.453	0.859

2003 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	115.99	61.23	474.08	6.41	43.906688	172.152	885.562	143.52	9.515
BH2	-33.5289	19.0436	47.541	68.687	180.717	1.391	47.970509	188.589	406.675	57.283	0.055
BH3	-33.9222	19.1096	10.332	3.209	22.097	2.735	9.6239134	37.835	36.852	3	0.055
BH4	-33.9375	19.11111	4.813	1.792	8.223	1.636	5.2035522	20.457	10.772	3	0.055
BH5	-33.03944	18.30583	50.2	9.3	123.6	1.56	29.709874	116.8	219.1	30.4	0.02
BH6	-33.88611	19.0875	11.639	8.378	25.127	1.48	20.321249	79.89	32.815	7.209	0.055
BH7	-33.11722	18.76111	74	138.4	1437.4	38.35	71.95996	282.9	2377.2	284.7	0.707
BH8	-33.3909	18.9963	36.684	204.748	1140.5	4.351	115.30382	453.3	2112.73	91.752	1.196
BH9	-33.14417	18.92083	116.743	62.293	475.208	6.641	43.916688	172.652	884.562	144.562	9.115
BH10	-33.04139	18.96139	13.659	15.236	122.883	6.377	19.226714	75.587	189.79	49.756	0.02
BH11	-33.8679	19.0407	1.009	2.29	10.88	0.383	1.0174614	4	20.09	3	0.904
BH12	-33.01861	18.96222	96.172	11.322	115.83	2.855	65.223348	256.416	197.564	5.186	0.02
BH13	-32.92028	18.295	35.645	11.733	119.624	2.599	27.655111	108.722	192.776	14.502	0.02
BH14	-33.8286	18.9417	3.35	3.887	26.501	1.813	2.8399892	11.165	51.369	3	1.845
BH15	-33.529	18.8505	68.556	62.683	491.314	2.924	30.83773	121.234	815.096	102.836	0.229
BH16	-33.6928	18.9005	52.7	85.129	319.334	0.391	47.90005	188.312	681.124	121.171	3.95
BH17	-33.5983	18.9787	27.512	34.178	110.863	2.943	11.475185	45.113	297.201	9.114	0.055
BH18	-33.3751	18.8849	15.281	19.5	44.812	1.512	20.775036	81.674	98.295	12.643	0.354
BH19	-33.4403	18.9335	19.987	35.965	318.96	1.622	48.576916	190.973	421.78	132.712	3.947
BH20	-32.91806	18.18417	63.076	69.374	1020.381	10.086	106.09579	417.1	1332.865	285.448	16.657

2004 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	172.686	69.541	466.139	7.596	60.344401	237.842	890.469	157.565	8.12
BH2	-33.5289	19.0436	46.06	68.039	185.137	1.376	47.861386	188.16	397.646	50.915	0.127
BH3	-33.9222	19.1096	15.023	3.25	20.351	2.131	10.885566	42.795	29.553	3	2.564
BH4	-33.9375	19.11111	4.238	1.043	7.404	1.813	4.1677764	16.385	10.008	3	0.436
BH5	-33.03944	18.30583	48.577	9.876	122.219	1.719	28.498841	112.039	201.624	31.621	0.02
BH6	-33.88611	19.0875	9.585	7.766	21.844	1.225	16.061901	63.145	27.112	9.133	0.055
BH7	-33.11722	18.76111	71.9	142.8	1406.4	37.92	64.939477	255.3	2365.2	296.3	0.746
BH8	-33.3909	18.9963	87.318	359.685	1827.508	7.391	81.582602	320.73	3509.11	313.698	0.186
BH9	-33.14417	18.92083	171.686	68.541	465.39	7.196	60.244401	236.842	889.469	159.565	8.212
BH10	-33.04139	18.96139	12.17	14.329	127.057	5.881	15.748777	61.914	190.781	42.474	0.055
BH11	-33.8679	19.0407	0.5	1.529	10.998	0.423	1.0174614	4	17.683	3	1.098
BH12	-33.01861	18.96222	71.79	10.788	109.021	2.152	46.114659	181.293	202.758	15.281	0.02
BH13	-32.92028	18.295	25.802	14.605	112.441	1.837	15.732243	61.849	184.882	28.56	0.02
BH14	-33.8286	18.9417	3.353	3.736	27.576	1.732	2.5823171	10.152	48.278	3	1.308
BH15	-33.529	18.8505	53.443	63.18	406.02	4.787	28.077103	110.381	778.38	108.43	1.96
BH16	-33.6928	18.9005	51.129	93.364	304.138	2.724	47.533255	186.87	610.503	119.57	3.988
BH17	-33.5983	18.9787	33.616	36.14	106.941	2.974	12.07625	47.476	297.349	3	2.139
BH18	-33.3751	18.8849	23.964	19.683	39.395	2.091	14.261248	56.066	93.323	14.502	12.205
BH19	-33.4403	18.9335	35.505	39.492	328.131	1.72	56.337857	221.484	435.052	144.857	0.294
BH20	-32.91806	18.18417	108.336	73.649	993.427	9.802	102.94166	404.7	1387.655	305.328	14.318

2005 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	146.641	63.68	473.107	7.28	58.02681	227.517	905.548	36.68	9.64
BH2	-33.5289	19.0436	48.391	71.349	178.085	1.168	46.54352	182.979	379.638	48.377	0.464
BH3	-33.9222	19.1096	14.097	3	18.403	2.146	11.29382	44.4	33.741	6.812	0.37
BH4	-33.9375	19.11111	5.708	1.167	7.43	1.963	6.572801	25.84	10.678	2	0.532
BH5	-33.03944	18.30583	47.248	9.39	121.405	1.69	27.40125	107.724	203.844	33.197	0.02
BH6	-33.88611	19.0875	19.947	10.322	24.387	1.526	25.50572	100.272	29.769	7.831	0.04
BH7	-33.11722	18.76111	58.4	134.7	1463.2	39.74	66.36392	260.9	2275.7	316.9	0.635
BH8	-33.3909	18.9963	88.331	307.722	1647.71	4.684	93.50038	367.583	3078.44	348.956	0.052
BH9	-33.14417	18.92083	144.641	62.568	453.07	7.228	58.12681	228.517	900.548	37.577	9.564
BH10	-33.04139	18.96139	10.619	16.479	131.369	6.136	18.17262	71.443	200.496	46.575	0.055
BH11	-33.8679	19.0407	0.5	2.542	10.87	1.644	2.059851	8.098	19.841	2	1.38
BH12	-33.01861	18.96222	67.827	10.23	123.911	2.358	41.19727	161.961	203.522	24.354	0.02
BH13	-32.92028	18.295	24.161	12.931	98.928	1.665	15.6974	61.712	187.626	30.206	0.02
BH14	-33.8286	18.9417	5.275	4.076	25.858	2.395	2.92393	11.495	51.277	2	1.685
BH15	-33.529	18.8505	27.956	41.274	250.898	6.628	45.49859	178.871	322.625	87.521	4.144
BH16	-33.6928	18.9005	48.781	92.012	297.849	2.652	44.88099	176.443	609.655	117.915	0.854
BH17	-33.5983	18.9787	29.353	35.182	105.425	3.168	8.498092	33.409	295.15	6.812	2.32
BH18	-33.3751	18.8849	15.951	21.602	43.436	1.74	10.70344	42.079	94.346	16.361	9.806
BH19	-33.4403	18.9335	24.139	31.021	229.95	1.313	31.87198	125.3	294.25	114.494	7.979
BH20	-32.91806	18.18417	107.165	74.551	994.333	10.108	99.82848	392.461	1386.174	275.731	11.664

2006 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	132.11	64.212	381.453	6.58	57.92417	224.789	684.7	118.572	11.8
BH2	-33.5289	19.0436	45.208	68.002	191.817	1.451	45.35182	178.294	406.972	52.543	1.302
BH3	-33.9222	19.1096	16.101	2.885	19.956	1.883	13.21428	51.95	35.509	5.789	0.04
BH4	-33.9375	19.11111	13.608	1.519	8.712	1.53	11.6652	45.86	18.06	7.519	0.279
BH5	-33.03944	18.30583	48.715	10.04	126.797	1.665	28.52529	112.143	207.983	30.566	0.02
BH6	-33.88611	19.0875	9.304	9.839	28.494	1.4	25.50572	72.874	34.331	2	0.04
BH7	-33.11722	18.76111	62.7	132.3	1388.7	29.02	76.30961	300	2303.5	291.8	0.42
BH8	-33.3909	18.9963	55.015	211.314	1157.198	4.046	118.5088	465.9	2075.47	184.939	0.08
BH9	-33.14417	18.92083	130.117	61.212	379.453	6.537	56.92417	223.789	674.7	118.572	11.368
BH10	-33.04139	18.96139	12.568	14.397	134.716	6.01	17.2124	67.668	192.164	43.665	0.055
BH11	-33.8679	19.0407	1.258	2.168	11.102	0.15	1.017461	4	19.852	2	1.642
BH12	-33.01861	18.96222	68.188	10.558	123.389	2.178	44.46281	174.799	221.548	22.719	0.042
BH13	-32.92028	18.295	26.154	13.498	121.77	1.891	15.45397	60.755	183.839	30.257	0.055
BH14	-33.8286	18.9417	3.328	3.533	29.107	1.7	2.177367	8.56	53.796	2	1.581
BH15	-33.529	18.8505	35.564	60.208	530.735	1.983	45.49859	139.115	856.528	116.278	6.491
BH16	-33.6928	18.9005	48.441	90.7	303.392	2.867	47.62788	187.242	566.678	110.893	5.813
BH17	-33.5983	18.9787	34.256	39.721	107.972	3.188	11.85648	46.612	307.4	7.41	0.455
BH18	-33.3751	18.8849	19.255	22.385	45.176	1.617	13.02554	51.208	94.113	36.458	10.064
BH19	-33.4403	18.9335	24.827	46.874	353.821	1.961	46.78262	183.919	484.647	156.998	1.72
BH20	-32.91806	18.18417	111.624	75.784	907.741	9.671	104.0354	409	1472.397	286.643	11.086

2007 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	124.24	51.453	340.94	6.12	55.77986	216.131	619.87	110.746	10.756
BH2	-33.5289	19.0436	43.097	62.084	172.279	1.28	48.53418	190.805	296.305	107.452	0.326
BH3	-33.9222	19.1096	17.031	3.369	23.784	2.498	15.15763	59.59	32.503	6.96	2.574
BH4	-33.9375	19.11111	20.237	2.71	12.522	2.336	21.93749	86.244	10.404	7.002	0.04
BH5	-33.03944	18.30583	48.577	9.876	122.219	1.719	28.49884	112.039	201.624	31.621	0.02
BH6	-33.88611	19.0875	2.837	1.633	8.723	0.665	1.017461	4	15.265	2	0.04
BH7	-33.11722	18.76111	62.3	138.6	1362.8	30.34	69.64524	273.8	2255.5	299.8	0.02
BH8	-33.3909	18.9963	23.429	175.277	1259.702	5.354	96.55149	379.578	2998.984	121.477	0.688
BH9	-33.14417	18.92083	126.424	51.3	341.984	6.172	55.07799	216.531	614.387	108.746	10.27
BH10	-33.04139	18.96139	13.774	15.431	127.993	6.004	15.18968	59.716	204.84	45.527	0.04
BH11	-33.8679	19.0407	1.102	1.81	10.864	0.41	1.017461	4	19.673	2	1.083
BH12	-33.01861	18.96222	70.963	11.296	118.411	2.223	42.79239	168.232	218.372	30.782	0.02
BH13	-32.92028	18.295	24.478	13.151	111.811	1.848	15.7882	62.069	185.821	36.439	0.055
BH14	-33.8286	18.9417	9.368	4.356	22.675	2.965	4.628432	18.196	46.627	15.349	2.364
BH15	-33.529	18.8505	39.4	60.6	576.9	3.9	38.9179	153	503.6	151.8	3.02
BH16	-33.6928	18.9005	46.123	83.194	275.596	2.506	44.57524	175.241	564.832	122.359	3.945
BH17	-33.5983	18.9787	29.694	37.584	107.887	3.053	9.071941	35.665	290.968	10.773	1.16
BH18	-33.3751	18.8849	18.835	20.892	47.645	1.814	13.37275	52.573	92.936	17.367	3.956
BH19	-33.4403	18.9335	20.96	44.115	318.332	1.889	42.08551	165.453	413.99	139.391	3.952
BH20	-32.91806	18.18417	94.223	71.254	873.158	8.916	103.2723	406	1347.182	278.781	15.279

2008 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	148.26	70.803	394.17	6.69	62.58669	244.119	777.064	153.372	7.978
BH2	-33.5289	19.0436	44.01	60.72	187.787	1.493	48.7392	191.611	299.526	53.929	0.04
BH3	-33.9222	19.1096	14.117	3.673	22.601	2.692	11.39582	44.801	33.389	6.782	1.928
BH4	-33.9375	19.11111	18.198	1.612	12.537	1.556	14.01019	55.079	11.247	7.838	0.04
BH5	-33.03944	18.30583	51.582	9.995	127.558	1.775	27.54319	108.282	210.841	36.288	0.02
BH6	-33.88611	19.0875	1.9	2.5	7.9	1	2.683555	10.55	13.538	4.131	0.426
BH7	-33.11722	18.76111	51.5	128.2	1375	26.49	60.9205	239.5	2261.5	320	0.091
BH8	-33.3909	18.9963	19.263	160.839	1241.867	6.954	99.01528	389.264	1873.818	134.431	1.101
BH9	-33.14417	18.92083	149.726	63.803	363.17	7.969	61.58669	242.119	757.064	173.372	7.78
BH10	-33.04139	18.96139	25.607	15.998	126.078	6.003	26.49317	104.154	192.991	50.69	0.04
BH11	-33.8679	19.0407	1.24	1.44	11.809	0.322	1.017461	4	16.849	11.91	1.435
BH12	-33.01861	18.96222	78.639	13.353	142.949	2.311	43.69005	171.761	234.419	41.377	0.04
BH13	-32.92028	18.295	25.572	12.981	105.542	1.894	16.07029	63.178	191.581	30.255	0.04
BH14	-33.8286	18.9417	4.096	3.068	28.193	2.062	2.118355	8.328	48.739	7.709	1.222
BH15	-33.529	18.8505	48.903	67.68	489.737	3.239	29.87089	117.433	863.931	134.29	0.04
BH16	-33.6928	18.9005	49.212	86.872	264.665	2.492	42.88396	168.592	562.344	109.259	5.148
BH17	-33.5983	18.9787	32.949	40.022	104.896	3.35	10.11128	39.751	288.609	7.169	2.156
BH18	-33.3751	18.8849	17.651	16.072	39.753	1.642	10.28654	40.44	91.692	12.948	3.996
BH19	-33.4403	18.9335	23.559	51.527	361.884	2.078	49.00857	192.67	507.427	151.979	3.77
BH20	-32.91806	18.18417	97.796	84.736	926.625	13.336	98.64212	387.797	1450.213	259.391	22.112

2009 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	138.94	60.74	403.3	7.8	58.28802	232.85	777.33	157.88	10.61
BH2	-33.5289	19.0436	47.054	52.323	161	1.7	53.37323	209.829	333.192	46.754	0.005
BH3	-33.9222	19.1096	8.888	3.677	21.8	3.47	8.538028	33.566	37.297	2.957	0
BH4	-33.9375	19.11111	14.945	1.927	12.7	2.92	15.99678	62.889	10.11	7.544	0.164
BH5	-33.03944	18.30583	51.932	10.476	124.244	1.817	27.36539	107.583	211.348	36.472	0.041
BH6	-33.88611	19.0875	2	1.7	9.8	0.3	2.034923	8	26	2.5	0.25
BH7	-33.11722	18.76111	66.4	136.8	1360.2	26.77	64.07463	251.9	2230.9	366	0.068
BH8	-33.3909	18.9963	16.818	194.105	1268.781	5.918	92.30588	362.887	1989.074	103.765	3.886
BH9	-33.14417	18.92083	133.594	65.074	393.3	7.8	59.7288	234.815	777.33	161.848	0.05
BH10	-33.04139	18.96139	12.236	15.399	124.689	5.799	15.03528	59.109	193.357	41.939	0.04
BH11	-33.8679	19.0407	20.877	0.75	10.2	1.38	1.017461	4	26.291	3.09	4.17
BH12	-33.01861	18.96222	65.488	11.646	129.513	2.262	38.68083	152.068	213.762	34.27	0.04
BH13	-32.92028	18.295	26.29	15.014	103.581	3.524	15.78871	62.071	192.352	31.472	0.025
BH14	-33.8286	18.9417	3	3.7	28.4	0.8	2.798019	11	77	2.5	1.54
BH15	-33.529	18.8505	58.126	68.852	457.7	7	33.30075	130.917	905.288	106.804	3.276
BH16	-33.6928	18.9005	51.737	93.643	298.3	4.1	47.43863	186.498	629.234	118.746	6.211
BH17	-33.5983	18.9787	35.017	45.41	109.9	4.1	10.88328	42.786	313.842	7.04	2.132
BH18	-33.3751	18.8849	21.3	20.9	43.9	1	15.26192	60	103	2.5	9.74
BH19	-33.4403	18.9335	19.3	38.9	333	0.8	34.33932	135	378	169	5.69
BH20	-32.91806	18.18417	94.197	83.849	970.3	12.1	102.4133	402.623	1491.002	318.002	13.893

2010 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	110.97	88.938	383	6.786	59.21516	243.157	525.47	169.627	2.653
BH2	-33.5289	19.0436	45.653	70.03	178	6.42	50.9298	200.223	231.861	56.623	0.005
BH3	-33.9222	19.1096	12.4	3.93	22.4	2.88	14.80406	58.2	36.5	3	1.99
BH4	-33.9375	19.11111	13.1	0.75	11.3	2.27	14.77863	58.1	13.4	4.48	0.372
BH5	-33.03944	18.30583	50.599	10.463	128.805	1.652	27.91584	109.747	211.142	33.465	0.02
BH6	-33.88611	19.0875	2.27	0.75	6.39	1.58	1.017461	4	16.3	3	0.756
BH7	-33.11722	18.76111	69.9	133.2	1342.7	28.62	66.28761	260.6	2236.9	303.5	0.053
BH8	-33.3909	18.9963	9.449	188.739	1106.783	6.346	93.96256	369.4	1963.222	57.138	6.651
BH9	-33.14417	18.92083	115.197	68.938	283	6.66	59.31215	233.177	520.47	169.727	2.63
BH10	-33.04139	18.96139	15.268	14.571	122.18	5.851	16.66983	65.535	194.738	40.28	0.04
BH11	-33.8679	19.0407	0.5	0.75	11	1.3	1.017461	4	21.3	3	1.15
BH12	-33.01861	18.96222	66.245	11.869	134.234	2.15	41.35599	162.585	235.296	37.912	0.04
BH13	-32.92028	18.295	26.918	14.386	109.727	3.463	16.44955	64.669	191.567	31.488	0.054
BH14	-33.8286	18.9417	1.59	2.02	27.9	2.02	2.251133	8.85	49.8	3	1.9
BH15	-33.529	18.8505	63.478	70.455	468.4	4.6	30.2621	118.971	858.485	107.893	1.587
BH16	-33.6928	18.9005	53.744	207.897	308.1	5.4	49.44786	194.397	654.506	114.071	3.506
BH17	-33.5983	18.9787	38.908	43.492	114	7.94	10.92932	42.967	227.476	7.053	0.784
BH18	-33.3751	18.8849	15	18.2	42.6	2.98	13.12525	51.6	99.5	13.1	8.82
BH19	-33.4403	18.9335	23.038	48.079	341	7.1	45.88013	180.371	549.757	144.635	4.26
BH20	-32.91806	18.18417	99.743	82.138	977.275	14.991	113.3976	445.806	1265.008	283.113	13.882

2011 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.9467	18.16194	143.47	66.66	338.369	8.56	60.92389	244.676	870.32	161.99	10.59
BH2	-33.5289	19.0436	50.03	61.181	182.137	3.002	53.43046	210.054	376.93	50.032	0.21
BH3	-33.9222	19.1096	13.961	5.107	24.47	2.966	11.33706	44.57	38.395	4.124	3.23
BH4	-33.9375	19.11111	5.357	2.959	11.049	2.457	4.053821	15.937	17.965	16.403	0.138
BH5	-33.0394	18.30583	48.999	10.16	119.394	1.743	28.43728	111.797	193.213	32.455	0.047
BH6	-33.8861	19.0875	1.724	1.64	7.799	1	0.635913	2.5	16.824	1.5	0.857
BH7	-33.1172	18.76111	64.023	126.686	1502.407	31.049	68.45506	269.121	2374	315.72	0.078
BH8	-33.3909	18.9963	13.178	188.476	1093.279	6.883	89.77418	352.934	1995.776	57.96	0.109
BH9	-33.1442	18.92083	140.757	67.366	388.369	8.656	62.92389	247.376	860.392	141.499	10.559
BH10	-33.0414	18.96139	11.351	12.653	117.556	5.507	15.42319	60.634	192.056	46.967	0.04
BH11	-33.8679	19.0407	3.929	0.75	7.029	1	2.706956	10.642	13.779	4.264	0.025
BH12	-33.0186	18.96222	52.2	8.2	88.3	2.6	33.6271	132.2	165.8	14.3	0.04
BH13	-32.9203	18.295	25.581	16.265	110.857	2.964	16.70214	65.662	197.592	28.531	0.065
BH14	-33.8286	18.9417	1.794	3.408	28.735	2.781	2.395104	9.416	49.105	1.5	1.255
BH15	-33.529	18.8505	39.4	60.6	576.9	3.9	38.9179	153	503.6	151.8	2.55
BH16	-33.6928	18.9005	46.049	97.674	438.19	26.803	42.32665	166.401	579.888	124.012	12.56
BH17	-33.5983	18.9787	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.89
BH18	-33.3751	18.8849	9.862	13.74	41.655	4.684	10.31095	40.536	75.038	1.5	16.821
BH19	-33.4403	18.9335	20.971	49.679	402.565	3.868	45.12823	177.415	606.903	162.558	4.966
BH20	-32.9181	18.18417	99.135	71.74	977.275	13.994	129.779	510.207	1541.098	294.646	17.104

2012 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.9467	18.16194	120.25	61.55	434.69	8.68	73.22355	287.013	950.476	165.782	10.55
BH2	-33.5289	19.0436	46.587	56.95	161.25	1	49.20418	193.439	324.479	45.945	0.025
BH3	-33.9222	19.1096	7.857	2.636	24.757	3.791	8.069232	31.723	35.637	1.5	3.251
BH4	-33.9375	19.11111	13.72	2	12.805	2.1	13.39259	52.651	12.864	3.568	0.246
BH5	-33.0394	18.30583	48.965	10.936	120.057	1.609	26.69539	104.949	207.08	33.857	0.02
BH6	-33.8861	19.0875	1.963	0.75	8.648	1	1.730193	6.802	15.329	1.5	0.697
BH7	-33.1172	18.76111	71.493	135.312	1374.616	24.365	70.20535	276.002	2258.378	327.354	0.232
BH8	-33.3909	18.9963	11.646	145.568	1155.31	8.444	70.62454	277.65	1976.623	5.919	8.181
BH9	-33.1442	18.92083	112.625	61.516	424.69	8.28	73.11224	287.43	923.476	126.782	10.44
BH10	-33.0414	18.96139	12.94	14.82	122.603	6.006	14.55377	57.216	190.792	44.594	0.04
BH11	-33.8679	19.0407	4.663	0.75	4.697	1	2.506771	9.855	6.495	1.5	0.025
BH12	-33.0186	18.96222	55.6	8.6	92.1	2.6	33.75428	132.7	185.5	13.5	0.04
BH13	-32.9203	18.295	28.8	15.3	120.7	3.2	15.92327	62.6	204.8	39.7	0.05
BH14	-33.8286	18.9417	5.476	2.019	29.642	2.868	3.339563	13.129	46.781	7.086	1.947
BH15	-33.529	18.8505	60.73	62.817	489.92	4.728	32.5547	127.984	834.347	108.776	2.317
BH16	-33.6928	18.9005	49.531	93.301	284.675	3.18	41.85735	164.556	563.088	117.415	7.073
BH17	-33.5983	18.9787	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.47
BH18	-33.3751	18.8849	15.973	20.363	44.383	2.379	11.92974	46.9	95.952	17.012	9.691
BH19	-33.4403	18.9335	18.179	39.712	349.39	3.08	42.4808	167.007	422.237	125.155	3.749
BH20	-32.9181	18.18417	99.588	94.168	1064.896	14.991	93.8191	368.836	1491.002	287.854	15.399

2013 Groundwater Data

Monitoring borehole	Latitude	Longitude	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3+NO2
BH1	-32.94667	18.16194	1750.31	71.199	548.81	9.76	65.64158	256.326	934.275	275.33	0.225
BH2	-33.5289	19.0436	36.43	61.472	160.655	2.79	51.98974	204.39	248.759	43.123	0.055
BH3	-33.9222	19.1096	10.959	4.386	19.258	4.122	9.446366	37.137	34.876	1.5	2.93
BH4	-33.9375	19.11111	7.683	0.75	15.652	2.791	9.326052	36.664	11.324	1.5	0.338
BH5	-33.03944	18.30583	51.238	8.566	123	2.57	31.19766	122.649	201.713	28.074	0.05
BH6	-33.88611	19.0875	1.204	0.75	11.991	2.223	3.435459	13.506	17.611	1.5	0.567
BH7	-33.11722	18.76111	58.793	130.112	1382.29	29.557	60.96069	239.658	2248.228	293.679	0.095
BH8	-33.3909	18.9963	6.209	157.756	1130.104	7.587	71.17397	279.81	2102.63	2	0.232
BH9	-33.14417	18.92083	190.1	71.104	547.81	8.956	65.25642	256.546	930.375	225.313	0.225
BH10	-33.04139	18.96139	11.368	14.548	134.477	5.907	14.95999	58.813	163.736	36.348	0.04
BH11	-33.8679	19.0407	12.319	1.584	2	1	8.242964	32.406	6.612	1.5	0.056
BH12	-33.01861	18.96222	60.2	10.1	104.7	2.3	34.84805	137	169.7	20.9	0.04
BH13	-32.92028	18.295	29.3	16.7	114.7	3.2	14.98212	58.9	206.8	38.9	0.05
BH14	-33.8286	18.9417	9.44	4.102	18.39	3.711	5.719914	22.487	35.828	16.43	0.909
BH15	-33.529	18.8505	37.474	60.693	588.32	3.12	42.13003	165.628	515.712	141.347	3.578
BH16	-33.6928	18.9005	42.781	87.883	296.89	4.107	41.83547	164.47	502.967	116.244	6.936
BH17	-33.5983	18.9787	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	3.1
BH18	-33.3751	18.8849	26.287	25.258	46.681	2.705	19.40808	76.3	97.238	27.676	6.538
BH19	-33.4403	18.9335	19.715	49.775	402.565	3.868	44.19674	173.753	508.747	136.756	5.295
BH20	-32.91806	18.18417	111.405	96.059	1014.64	13.523	128.4563	505.007	1417.597	285.013	12.98

APPENDIX B (i)

INSITU AND LABORATORY DATA ANALYSED AT STELLENBOSCH UNIVERSITY

2016 INSITU

Sample ID	Latitude	Longitude	TDS (ppm)	Salinity (ppm)	pH	Temperature °C	Elecrival Conductivity µS
T1	33° 52' 56.73" S	19° 2' 49.30" E	57	41	6.9	17.7	107
T2	33° 13' 5.91" S	18° 58' 27.49" E	523	298	7.2	17.8	803
T3	32° 54' 35.63" S	18° 39' 35.87" E	390	293	7.2	18	618
S1	33° 54' 13.57" S	19° 3' 15.90" E	15	16	6	15.5	27
S2	33° 54' 5.21" S	19° 3' 12.43" E	25	8	6.05	15.8	37
S3	33° 52' 39.13" S	19° 2' 2.96" E	22	25	6.7	17.2	32
S4	33° 52' 35.85" S	19° 1' 54.90" E	46	25	6.7	17.3	47
S5	33° 45' 48.34" S	18° 58' 27.70" E	36	22	7.72	17.3	55
S6	33° 45' 6.50" S	18° 58' 7.14" E	68	52	7.17	19.4	104
S7	33° 44' 54.07" S	18° 58' 3.22" E	52	34	7.17	19.7	81
S8	33° 44' 46.29" S	18° 58' 2.54" E	48	46	6.81	18.7	60
S9	33° 44' 34.53" S	18° 58' 5.07" E	72	53	7.15	18.2	107
S10	33° 44' 22.20" S	18° 58' 9.83" E	46	55	7.22	19.3	119
S11	33° 43' 34.99" S	18° 58' 31.36" E	78	58	7.22	19.7	112
S12	33° 42' 48.73" S	18° 58' 20.85" E	102	59	6.97	20	127
S13	33° 42' 26.50" S	18° 58' 26.35" E	96	72	6.96	19.5	137
S14	33° 39' 1.44" S	18° 58' 3.89" E	135	90	6.95	19.2	180
S15	33° 37' 43.36" S	18° 58' 33.78" E	147	103	6.96	19.2	216
S16	33° 35' 23.06" S	18° 57' 2.66" E	151	74	6.66	15.3	243
S17	33° 33' 57.98" S	18° 57' 6.00" E	102	75	6.83	15.8	150
S18	33° 26' 57.20" S	18° 57' 18.73" E	84	68	6.73	17.2	134
S19	33° 20' 32.15" S	18° 58' 45.90" E	191	148	7.07	19.1	212
S20	32° 58' 23.72" S	18° 44' 54.63" E	750	569	7.58	20.2	1210
S21	32° 55' 27.75" S	18° 40' 39.27" E	1022	506	7.44	21.2	1215
S22	32° 47' 19.35" S	18° 10' 9.89" E	6970	4750	7.44	20.7	10500
S23	32° 47' 27.92" S	18° 10' 9.97" E	11420	1780	8.85	22.7	11820

2017 INSITU

Sample ID	Latitude	Longitude	TDS (ppm)	Salinity (ppm)	pH	Temperature °C	Elecrival Conductivity µS
T1	33° 52' 56.73" S	19° 2' 49.30" E	104	83	8.6	14.1	153
T2	33° 13' 5.91" S	18° 58' 27.49" E	454	361	6.9	18.2	708
T3	32° 54' 35.63" S	18° 39' 35.87" E	DRY				
S1	33° 54' 13.57" S	19° 3' 15.90" E	90	55	9.9	14.5	47
S2	33° 54' 5.21" S	19° 3' 12.43" E	23	28	8.33	14.5	52
S3	33° 52' 39.13" S	19° 2' 2.96" E	47	33	5.32	13.9	66
S4	33° 52' 35.85" S	19° 1' 54.90" E	52	36	8.1	13.9	77
S5	33° 45' 48.34" S	18° 58' 27.70" E	66	45	8.1	14	90
S6	33° 45' 6.50" S	18° 58' 7.14" E	72	53	7.95	14.5	105
S7	33° 44' 54.07" S	18° 58' 3.22" E	67	47	7.89	14.6	59
S8	33° 44' 46.29" S	18° 58' 2.54" E	102	70	7.51	14.7	13.5
S9	33° 44' 34.53" S	18° 58' 5.07" E	60	45	7.4	14.5	89
S10	33° 44' 22.20" S	18° 58' 9.83" E	68	49	7.5	14.7	105
S11	33° 43' 34.99" S	18° 58' 31.36" E	78	63	7.5	15	125
S12	33° 42' 48.73" S	18° 58' 20.85" E	87	67	7.44	15.6	133
S13	33° 42' 26.50" S	18° 58' 26.35" E	128	108	8.08	16.6	202
S14	33° 39' 1.44" S	18° 58' 3.89" E	164	142	7	17.2	254
S15	33° 37' 43.36" S	18° 58' 33.78" E					
S16	33° 35' 23.06" S	18° 57' 2.66" E					
S17	33° 33' 57.98" S	18° 57' 6.00" E	162	140	6.84	16.9	267
S18	33° 26' 57.20" S	18° 57' 18.73" E	172	148	7.15	17.5	275
S19	33° 20' 32.15" S	18° 58' 45.90" E	180	145	7.07	17	180
S20	32° 58' 23.72" S	18° 44' 54.63" E	666	495	8.11	17.1	990
S21	32° 55' 27.75" S	18° 40' 39.27" E	1082	814	7.62	17.7	1758
S22	32° 47' 19.35" S	18° 10' 9.89" E	DRY				
S23	32° 47' 27.92" S	18° 10' 9.97" E					

APPENDIX B (ii)

CHEMICAL ANALYSIS FOR WET AND DRY SEASON IN 2016 AND 2017

ICP-MS Laboratory
CAF Central Analytical Facilities
STELLENBOSCH UNIVERSITY
Agilent Technologies
Authorized Partner Laboratory

		Accuracy (%)	T1	T2	T3	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23
Ca	mg/L	92.8	6.87	17.01	6.74	1.12	1.08	2.89	4.14	5.76	5.88	5.84	5.93	6.71	6.70	6.64	8.86	8.73	9.12	9.32	9.86	9.99	9.83	10.92	23.53	29.95	109.50	841.40
Fe	mg/L	95.7	0.29	0.20	0.46	0.19	0.17	0.22	0.24	0.18	0.17	0.17	0.17	0.16	0.17	0.19	0.12	0.17	0.18	0.20	0.38	0.73	0.33	0.39	0.03	0.09	0.01	0.05
K	mg/L	91.2	1.64	3.46	1.50	1.57	0.26	0.81	1.06	3.08	2.98	3.07	3.06	3.19	3.27	3.25	4.22	4.06	4.46	4.46	4.59	5.11	4.91	5.05	6.08	6.73	65.74	1201.0
Mg	mg/L	94.9	2.20	26.66	9.81	0.48	0.47	1.15	1.48	2.40	2.41	2.42	2.44	2.59	2.62	2.56	3.40	3.25	3.60	3.66	4.66	5.23	5.51	7.10	29.82	39.11	293.00	5215.0
Na	mg/L	94.2	11.19	103.60	61.79	3.05	3.13	6.47	8.20	10.92	10.82	11.12	11.19	11.87	11.90	11.57	17.67	17.24	22.29	22.76	29.03	33.68	34.81	41.48	161.60	201.50	2163.0	40250.0
P	mg/L	99.8	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.14	0.11	0.11	0.11	0.11	0.09	0.08	0.20	0.19	0.32	0.32	0.25	0.29	0.24	0.18	0.02	0.03	0.09	1.88
S	mg/L	99.9	2.00	18.27	4.42	0.40	0.40	0.95	1.38	1.92	1.96	1.93	1.94	2.09	2.15	2.09	3.16	2.97	3.53	3.55	4.36	4.70	4.46	5.09	3.09	3.07	3.05	3.03
Si	mg/L	99.8	3.91	1.57	3.64	1.00	0.99	2.11	2.65	2.40	2.48	2.48	2.50	2.67	2.71	2.81	2.92	2.85	3.12	3.11	3.37	4.22	3.24	3.40	2.13	2.35	2.50	1.48
Sr	mg/L	97.7	0.04	0.27	0.06	0.01	0.01	0.02	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.05	0.06	0.06	0.07	0.08	0.08	0.10	0.29	0.37	1.77	21.45
		Accuracy (%)	**T 1**	**T 2**	**T 3**	**S 1**	**S 2**	**S 3**	**S 4**	**S 5**	**S 6**	**S 7**	**S 8**	**S 9**	**S 10**	**S 11**	**S 12**	**S 13**	**S 14**	**S 15**	**S 16**	**S 17**	**S 18**	**S 19**	**S 20**	**S 21**	**S 22**	**S 23**
Li	µg/L	97.7	0.69	2.38	0.59	0.86	0.81	0.66	0.68	0.64	0.59	0.61	0.64	0.66	0.62	0.63	0.87	0.92	1.27	1.35	1.44	1.75	1.19	1.35	3.08	3.89	11.36	161.85
Be	µg/L	95.6	0.03	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.06	0.02	0.02	<0.0030	0.01	0.02	<0.0030
B	µg/L	99.7	12.28	25.39	53.60	5.85	5.59	8.95	9.65	15.07	14.83	15.21	15.35	15.06	15.77	15.32	18.55	18.83	20.79	21.93	24.74	26.80	25.31	26.68	91.77	135.85	689.35	5052.27
Al	µg/L	97.4	144.42	23.68	47.68	97.52	91.38	101.54	113.86	112.21	104.59	104.18	104.42	85.68	158.27	123.52	38.40	100.01	194.79	238.76	673.26	2006.31	296.53	242.34	13.40	47.91	< 0.1	< 0.1
V	µg/L	99.5	0.37	0.14	0.17	0.14	0.13	0.19	0.25	0.45	0.44	0.42	0.38	0.42	0.44	0.45	0.37	0.62	0.74	0.72	1.30	1.98	0.96	0.92	0.29	0.39	2.16	3.03
Cr	µg/L	98.4	0.17	0.14	0.15	0.09	0.09	0.13	0.13	0.17	0.17	0.17	0.16	0.16	0.18	0.20	0.19	0.23	0.35	0.38	0.63	1.13	0.40	0.42	0.15	0.19	0.29	1.04
Mn	µg/L	96.8	0.56	3.10	39.48	60.23	23.99	2.27	0.91	0.60	0.39	0.32	0.38	0.30	0.35	0.38	0.23	0.35	0.47	0.51	1.83	2.96	2.33	7.85	10.18	92.14	2.77	103.59
Fe	µg/L	99.1	257.61	257.39	483.27	151.56	142.11	195.27	233.70	177.83	166.65	172.27	161.14	151.79	169.34	200.14	144.18	213.83	250.89	267.58	562.62	993.98	386.26	479.37	38.98	114.04	1.27	52.47
Co	µg/L	94.5	0.03	0.26	0.08	0.05	0.02	0.02	0.02	0.05	0.06	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.07	0.07	0.12	0.20	0.11	0.15	0.17	0.32	0.04	0.03
Ni	µg/L	99.2	0.22	1.96	0.49	0.10	0.08	0.24	0.15	0.30	0.30	0.32	0.30	0.36	0.34	0.48	0.62	0.58	0.67	0.69	0.80	1.10	0.74	0.90	1.05	1.11	1.11	1.83
Cu	µg/L	93.3	0.61	1.04	0.38	0.43	0.19	0.52	0.39	0.84	0.83	0.90	0.78	1.02	0.90	1.10	1.07	1.15	1.27	1.26	1.32	1.70	0.96	1.08	1.43	1.94	5.27	3.85
Zn	µg/L	99.8	2.42	1.62	2.15	1.07	0.46	2.84	1.52	1.44	2.25	2.28	2.25	3.64	3.55	4.72	8.36	7.56	7.17	6.70	3.34	4.78	2.03	1.77	3.42	1.39	< 0.05	1.96
As	µg/L	87.8	0.35	0.48	0.24	0.11	0.12	0.19	0.26	0.36	0.37	0.36	0.37	0.36	0.38	0.40	0.69	0.71	1.02	1.05	1.18	1.34	0.90	0.96	0.62	0.71	1.60	9.62
Se	µg/L	96.7	0.11	0.19	0.10	0.06	0.07	0.10	0.09	0.10	0.12	0.10	0.10	0.12	0.13	0.12	0.15	0.14	0.17	0.16	0.17	0.24	0.15	0.16	0.37	0.46	0.02	0.26
Mo	µg/L	99.7	0.04	0.04	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.03	0.03	0.03	0.06	0.04	0.07	0.06	0.07	0.08	0.09	0.11	0.05	0.06	0.07	0.19	3.78	19.33
Cd	µg/L	97.6	< 0.005	< 0.005	0.007	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.052	0.109
Sb	µg/L	97.8	0.58	0.24	0.48	0.21	0.24	0.54	0.51	0.34	0.43	0.36	0.39	0.47	0.39	0.35	0.43	0.47	0.51	0.64	0.45	0.38	0.38	0.31	0.31	0.29	0.43	0.94
Ba	µg/L	98.5	16.13	22.31	12.81	2.47	2.37	7.66	10.51	10.36	11.44	11.53	12.10	13.03	12.49	12.95	12.72	11.21	12.13	12.32	14.22	18.68	14.10	18.62	28.81	37.42	19.56	79.41
Hg	µg/L	95.0	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	µg/L	100.0	0.12	0.05	0.06	0.07	0.05	0.07	0.07	0.10	0.11	0.11	0.14	0.10	0.14	0.17	0.17	0.30	0.51	0.61	0.51	0.89	0.37	0.41	0.03	0.06	< 0.005	< 0.005

CAF Central Analytical Facilities
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Component Summary For Amount mg/L

#	Sample Name	chloride	nitrite	bromide	nitrate	phosphate	sulphate
3	T1	10.0			58.3		2.1
5	T2	94.3			66.6		45.3
7	T3	57.8			57.5		4.9
9	S1	3.8			55.1		
11	S2	2.7			59.1		
13	S3	6.4			67.8		
15	S4	7.4			60.5		
17	S5	9.2			69.2		
19	S6	10.6			78.8		
21	S7	9.4			76.9		
23	S8	9.6			76.7		
26	S9	10.8			74.5		
28	S10	10.7			86.3		
30	S11	10.5			72.2		
32	S12	15.0			87.6		2.6
34	S13	14.7			83.0		3.0
36	S14	18.2			84.9		3.4
38	S15	17.7			78.3		3.4
40	S16	23.8			83.8		7.0
42	S17	27.3			92.1		7.6
44	S18	29.6			85.6		8.4
46	S19	37.3			91.9		7.9
48	S20	162.7		3.6	86.3		49.1
50	S21	219.0		5.0	69.5		67.4
51	S22	438.7					64.2
52	S23	2530.2		23.2	29.8		914.3

ICP-MS Laboratory
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		QC Recovery (%)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S17	S18	S19	S20
Li	**µg/l**	***102***	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Be	**µg/l**	***102***	<0,03	<0,03	0.05	<0,03	0.03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	0.03	<0,03	<0,03	0.03	0.06	0.07	<0,03
B	**µg/l**	***109***	5.49	5.27	21.34	7.53	9.08	9.44	9.71	9.80	9.21	9.48	9.57	10.11	15.85	16.89	18.05	19.87	23.35	65.38
Al	**µg/l**	***96***	37.6	54.4	568.4	206.7	122.2	102.0	116.3	164.7	134.0	135.6	145.9	274.5	137.9	147.3	334.8	969.3	1453.7	36.7
V	**µg/l**	***103***	0.10	0.11	1.09	0.28	0.41	0.38	0.41	0.48	0.43	0.43	0.46	0.71	0.60	0.68	1.30	2.00	2.57	0.22
Cr	**µg/l**	***96***	0.09	0.09	3.56	0.17	0.31	0.21	0.18	0.39	0.28	0.28	0.38	0.45	0.78	0.56	0.66	1.08	1.23	0.13
Mn	**µg/l**	***95***	21.14	26.73	39.83	19.23	11.20	9.33	12.27	15.01	10.20	11.63	9.88	12.96	18.18	16.98	21.04	15.76	23.77	65.67
Fe	**µg/l**	***103***	104.5	151.3	542.7	188.0	206.0	183.0	218.9	266.8	209.2	242.3	209.7	347.0	281.0	267.6	527.4	850.2	1145.9	186.8
Co	**µg/l**	***104***	0.04	0.03	0.53	0.08	0.18	0.09	0.09	0.12	0.13	0.10	0.09	0.18	0.13	0.12	0.19	0.24	0.37	0.31
Ni	**µg/l**	***94***	<1,0	<1,0	6.96	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	1.04	1.13	1.02	1.14	1.53	<1,0
Cu	**µg/l**	***98***	2.05	0.39	33.78	0.89	1.28	1.21	1.32	3.90	1.44	1.61	2.45	1.76	3.15	2.39	2.27	2.18	3.87	1.31
Zn	**µg/l**	***101***	4.53	1.25	376.28	7.00	4.93	8.94	10.06	28.70	10.69	16.29	23.58	20.64	31.93	21.02	13.96	10.49	14.65	3.20
As	**µg/l**	***98***	0.15	0.16	1.41	0.20	0.33	0.31	0.29	0.38	0.30	0.33	0.35	0.50	0.79	0.86	1.36	1.53	1.69	0.91
Se	**µg/l**	***98***	<0,5	<0,5	0.53	<0,5	0.57	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	0.57	<0,5	<0,5	0.75	0.50	0.87
Sr	**µg/l**	***96***	9.03	9.01	86.14	12.85	15.54	16.98	17.31	19.16	17.05	18.42	20.40	23.34	40.31	42.36	49.07	53.74	59.39	200.37
Mo	**µg/l**	***100***	0.10	0.07	0.34	0.06	1.00	0.38	0.24	0.18	0.18	0.13	0.13	0.13	1.08	0.50	0.39	0.36	0.30	0.27
Cd	**µg/l**	***102***	0.01	0.01	0.57	0.02	0.04	0.02	0.02	0.04	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.03	0.01
Sb	**µg/l**	***90***	0.58	0.73	1.49	0.83	0.78	0.69	0.83	0.92	0.85	0.58	0.69	0.77	0.64	0.70	0.79	0.83	0.93	0.41
Ba	**µg/l**	***99***	2.06	1.96	31.08	4.76	7.11	7.47	7.64	9.67	7.79	8.15	8.75	9.94	11.73	10.54	11.39	13.18	17.03	25.70
Hg	**µg/l**	***104***	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02
Pb	**µg/l**	***98***	0.11	0.11	16.82	0.62	0.51	0.44	0.59	1.64	0.66	0.82	0.95	1.23	1.35	1.20	1.27	1.25	1.99	0.14
Ca	**mg/l**	***107***	1.10	1.07	15.41	1.80	2.59	2.88	2.95	3.44	2.86	2.95	3.30	3.75	6.92	7.65	7.96	8.53	9.12	17.34
K	**mg/l**	***101***	0.45	0.35	5.19	0.94	1.86	2.00	2.04	3.11	2.08	2.13	2.77	2.37	4.87	5.49	6.65	7.04	8.58	4.52
Mg	**mg/l**	***112***	0.59	0.58	2.72	0.93	1.26	1.34	1.36	1.39	1.29	1.23	1.33	1.40	2.08	2.31	2.51	2.95	3.31	21.14
Na	**mg/l**	***107***	4.07	3.88	19.97	6.60	8.14	8.50	8.41	8.75	8.02	8.37	9.19	9.30	19.32	21.43	23.94	24.96	30.76	136.60
P	**mg/l**	***104***	<0,02	<0,02	0.32	<0,02	0.06	0.05	0.07	0.07	0.05	0.06	0.06	0.06	0.38	0.52	0.37	0.42	0.50	0.03
Si	**mg/l**	***102***	1.08	1.11	1.03	1.03	1.21	1.41	1.42	1.40	1.45	1.31	1.45	1.78	1.91	1.99	2.15	3.06	3.83	0.49