GROUNDWATER AND SURFACE WATER INTERACTION IN THE UITENHAGE ARTESIAN BASIN, EASTERN CAPE, SOUTH AFRICA: CASE STUDY OF THE SWARTKOPS AND COEGA AQUIFER

By

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Abstract

The state of water quality in the Swartkops River catchment in the Uitenhage area, Eastern Cape Province, South Africa, continues to be degraded by anthropogenic activities, which include municipal waste water, industrial waste and agricultural runoff. The study area consists of two aquifers (Swartkops and Coega) that are separated by the fault (Coega fault). In the study area there are two main rivers, namely: Swartkops River and Coega River, which are situated in the Swartkops Aquifer and Coega Aquifer, respectively. Most of the degrading anthropogenic activities are situated in the vicinity of the Swartkops River. The focus of the study was on the pollution of the stream water and aquifer (groundwater), with particular emphasis on the groundwater management. The study objectives were to establish the relationship between groundwater levels and surface topography using Bayesian interpolation method and groundwater and surface water interaction using environmental isotope and hydrogeochemical techniques. The bacteriological assessment was also conducted to determine if hydraulic connections exist between groundwater and the polluted streams. The results of the Bayesian Interpolation Method indicated that there was a strong relationship between the groundwater level elevation and surface topography with the correlation coefficient of 0.9953. The results also indicated that the fault is permeable; hence it did not have influence on groundwater circulation; however, groundwater does not flow from Swartkops River to Coega Aquifer due to groundwater flow gradient. The environmental isotope results indicated that both Swartkops Aquifer and Swartkops River were characterised by heavy isotopes signatures, which indicated the correlation between the two water components. The results further showed that the Swartkops River was recharging the Swartkops aquifer. However, no correlation was established between Swartkops River and Coega aquifer due to flow gradient. Although the flow gradient allows the flow of groundwater from Coega Aquifer to Swartkops Aquifer, Coega aquifer is a Government Water Controlled Area, which could have a very low to none impact on the other aquifer. Piper diagram and stiff diagrams indicated one water type found in the Swartkops and Coega aquifers, which was: Na-Cl type. The water in the Coega aquifer indicated high salinity in the chemical properties, which was typical old marine water derived from deep groundwater source. It was noted that the electrical conductivity values in the Waste Water Treatment Work were closest to those of the Swartkops River and Aquifer, which was in central to those of Coega Aquifer. The bacterial analysis results indicated that during the wet season most of the bacterial counts were high as compared to dry season. It was noted; however, that during the wet season the bacterial counts appeared similar in both aquifers. It is unlikely that the similarities emanated from the interaction of

the two aquifers as the analysis of the results indicated that the bacterial counts found in the Coega Aquifer emanated from the farming activities. The study concluded that the fault act as a pathway for migration of groundwater flow. It was established that the groundwater only flows from Coega Aquifer to Swartkops Aquifer due to difference in the hydraulic gradient.

Dedication

I dedicate this to my lovely kids, Ezempumelelo and Minenhle as well as to my wife, Nosabelo, from whom I stolen our valuable time, which we were supposed to have spent together. I am forever indebted to them.

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Special gratitude's also goes to Mr Mike Buttler, iThemba Labs, Gauteng, for environmental isotope sample analysis. The Department of Water and Sanitation is also acknowledged for funding my study through to this end.

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Acronyms

DWS	:	Department of water and Sanitation
DWA	:	Department of water Affairs
DWAF	:	Department of water and forestry.
GWCA	:	Government Water Control Area
RQIS	:	Resource Quality Information Services
WWTW	:	Waste Water Treatment Works
CMA’s	:	Catchment Management Agencies
TMG	:	Table Mountain Group
TMS	:	Table Mountain Sandstone
UAA	:	Uitenhage Artesian Aquifer
UAB	:	Uitenhage Aquifer Basin
CRA	:	Coaga Ridge Aquifer
NWRS2	:	Second Edition of the South African National Water Resource Strategy
EC	:	Electrical Conductivity
^{18}O	:	Environmental isotopes of oxygen
^{2}H or D	:	Environmental isotopes of hydrogen/Deuterium
^{3}H	:	Tritium
TU	:	Tritium Unit
T	:	Temperature
Cl^{-}	:	Chloride
O	:	Oxygen
H	:	Hydrogen
DIC	:	Dissolve Inorganic Carbon
TDS	:	Total Dissolved Solid
IAEA	:	International Atomic Energy Agency
GNIP	:	Global Isotopic database
GMWL	:	Global Meteoric Water Line
LMWL	:	Local Meteoric Water Line
MPN	:	Most Probable Number
mbgl	:	meters below groundwater level
cfu	:	colony forming unit (s)

1. CHAPTER ONE: INTRODUCTION

1.1 General overview

The study is about applying the environmental tracer's method (hydrochemistry, stable isotopes of oxygen and hydrogen, and radioactive isotopes of tritium) and bacteriological analysis of the water from Uitenhage spring, Swartkops River and boreholes. As the Uitenhage spring supplies water to the nearby communities, it raises a concern for it to be in vicinity that is prone or exposed to pollution. The industries and agricultural sectors also require the stringent water quality standards for their activities and therefore, the water resources in the area should be protected against pollution. The study is meant to improve the knowledge of the groundwater and surface water resources in the area by establishing the interaction between two water sources. The conceptual model was developed in this study area.

1.2 Background

The water resources in Africa are facing the challenge of degrading quality and quantity, it has an impact in the economy as well (Ashton, 2002). From the South African perspective, the pollution to the water resources is of growing concern and needs to be controlled (SWLR, 1995) as well as their quality needs to be protected (Dallas and Day, 1993; Jagals *et al*. 1997; Quilbell *et al*. 1997); particularly, in case when polluted streams can also be the main sources of contamination to aquifers (Winter *et al*. 1998). The effects of contaminants may not be revealed for quite a number of years after it has entered the groundwater system.

South Africa, being a water scarce country, is predominantly dependent on surface water resources (Davies and Day, 1998). The water resource of South Africa is prone to pollution primarily from sewage treatment works, agriculture and industrial waste water that contains metals (Vollenwider, 1998). The second edition of the South African National Water Resource Strategy, (NWRS2, 2013) clearly indicates that, water resources need to be sustained for industrial , agricultural and domestic water use as well as for ecosystem functioning. The contamination of streams might results in the contamination of the aquifers (Pinder *et al*. 2006); but it would be unlikely that the aquifers could be remediated for domestic water use (Kalbus *et al*. 2006; Feinberg, 2015).

The Department of Water and Sanitation (DWS) – a government water custodian – acknowledges that South Africa is facing numerous water challenges and concerns, which include water accessibility, degradation of the environment and resource pollution, and the inefficient use of water in different sectors. The DWS is responsible for the implementation of policies and strategies related to South African water resources management to ensure that everyone has access to good quality water and to ensure environmental protection.

The DWS has a directorate responsible for water quality issues in South Africa – the Resource Quality Information Services (RQIS). The RQIS has both surface water and groundwater monitoring points across the country. The chemical components of water quality that the RQIS is monitoring is microbiological, and macro and micro chemical elements. Generally, the overall conclusion from the interpretations gathered from the currently accumulated chemical data is that the South African water resources state of quality is deteriorating. This deterioration can be associated to the increasing human developments impacts across the country. The escalation of bacteriological content in water resources is associated to the inadequate management of Waste Water Treatment Works (WWTW) by the municipalities in most parts the country. On the other hand, the escalation of macro and micro chemical content of contaminants in water resources can be associated with the improper management of the final effluent from the industries. The Uitenhage area, in the Eastern Cape Province of South Africa, is not different from the above mentioned circumstances. The Uitenhage area consists of two river catchments, *viz.* Coega River and Swartkops River catchments.

The Coega River catchment is found at the northern boundary of the study area, which stretches from Groot Winterhoek Mountains, at the western part of the Uitenhage spring to the sea – Blue Water Bay, at the north east of Port Elizabeth. The catchment consists of the shallow aquifer, which is called Coega aquifer. The aquifer is a source of artisan groundwater and is economically significant for bulk water supply for Uitenhage, Amanzi Estates, Sandfontein, Coega Kop and Wells Estate (Maclear, 2001). The community of Uitenhage area depends on Uitenhage spring for domestic water supply. There is also an intensive irrigation (citrus fruit and Lucerne) taking place in the area under investigation.

The Swartkops River catchment is found at the southern boundary of the study area, which covers the Nelson Mandela Metropolitan Municipality, which includes Uitenhage, Kwanobuhle, Despatch and part of the Port Elizabeth municipal areas. There has been a progressive degradation of the Swartkops River water quality due to contaminants from industries, agriculture, municipalities, urban, and rural or informal settlements. The main contributors to the river pollution around the area are industrial and municipal wastes. They are discharging the effluents directly into the river. The characteristic of contaminants that pollute the river are represented by bacteria, nitrates, and industrial chemicals (DWAF, 1996; Taljaard *et al*. 1998). Water pollution raises concerns to the community and other water stakeholders of the Uitenhage area and therefore, the protection of water resources in this area is essential. Currently, there is no monitoring of wastes that is being discharged into the Swartkops River, although irrigation activities rely entirely on it as key for water supply. Several studies conducted in the Uitenhage area have made some recommendations on the protection of water resources in the areas. However, there is still a lack of implementation of these recommendations and less compliance with the legislation. This is because there is no adequate monitoring network established to record the information that needs to be reported to DWS (Eastern Cape Groundwater Plan, 2010). As a result, sustainable planning of the water resources in the areas is jeopardised. The DWS has established Catchment Management Agencies (CMA's) that are responsible to ensure that sustainability is achieved and enforcing compliance. The CMA's are tasked to set several catchment monitoring and management strategies to safeguard the availability of groundwater and surface water resources for future developments in the country. Monitoring and enforcing compliance should close the gap of understanding groundwater use, and impose penalties for water users that do not comply with the policies and management strategies.

The industries are generally issued with licenses to discharge the waste into the river, but there seems to be less compliance with license conditions in the Uitenhage area. Thus, the pollution has not been monitored for years. The Water Quality Management Plan is one of the main recommendations from the previous studies and condition of the license issue. The plan states that there should be a continuous water quality monitoring, i.e. drilling of monitoring boreholes by industries, data collection (water samples) and supply to DWS for analysis to ensure compliance. Due to the unavailability of this information, the extent of pollution in the groundwater system is not known. Therefore, the current study intends to investigate the impact of pollution in the groundwater system in order to establish the rehabilitation and mitigation measures.

Given the fact that there are a large number of groundwater users within the Table Mountain Group (TMG) aquifer in the region, it resulted in various essential investigations conducted to improve planning and management of the groundwater from the aquifers (Maclear, 2001). According to Maclear (2001), groundwater from this basin was extensively exploited in the early 21stcentury, which caused drastic decrease in the yield of the springs and water levels in the boreholes. As a result, the farmers were also affected by the groundwater over-exploitation until the investigations of the possible factors were requested. The Uitenhage Artesian Aquifer (UAA) was then declared in 1957 as a Government Water Control Area (GWCA) to minimize abstraction to sustainable rates (Venables, 1985).

Across the world, water pollution in the aquifers is mainly caused by the anthropogenic activities and it is a main concern in the groundwater resource management (Egboka *et al*. 1989). Considering the activities from industries, municipalities and agriculture that are taking place in the catchment, the UAA is also susceptible to water pollution. Environmental isotopes (stable isotopes of oxygen and hydrogen, and radioactive isotopes of tritium) have been proved to be useful techniques to understand and in the prediction of spatial distribution and temporal changes in the aquifer, tracing pathways and assessment pollution, and aquifer planning and management; it is also useful in the investigation of surface and groundwater interconnections (De Vries and Simmers, 2002; Yang *et al*. 2012). Hydrochemical variables have also significant role in groundwater studies, because chemical parameters assist in the classification and assessment of water quality (Sadashivaiah *et al*. 2008). The bacteriological assessment is helpful to determine if there are any hydraulic connections between groundwater and the polluted surface water because where groundwater systems are recharged by surface water, microbials can also enter the groundwater systems. However, a majority of wells, if properly constructed, are bacteria-free and the soil could act as a barrier to contamination of the aquifers.

Important works done conducted in the Uitenhage area includes Parsons (1983); Talma *et al*. (1982), Talma *et al*. (1984), Venables (1985), Maclear (1993), Maclear (1995), Vogel *et al*. (1999), and Binning and Baird (2001). Similar studies that involved the interconnection between groundwater and surface water have also been conducted worldwide, such as Egboka *et al*. 1989; Ekiye and Luo, 2010; Kipkemboi, 2011; Maheshwari *et al*. 2011; Batisani, 2012; Yang *et al*. 2012; Bello *et al*. 2013; Miller *et al.* 2013; Scholz, 2014; West *et al*. 2014; King *et al*. 2015 and Celiker, 2016 are some of them. The literature survey of the study area revealed the need to conduct this study, due to unavailability of the information with regard to groundwater and surface water chemistry; owing to the fact that the pollution of Swartkops River had raised some concerns to residence of Uitenhage area (Binning and Baird, 2001). The literature suggests that there is no knowledge on whether surface water and groundwater are connected and if the interconnection exist; to what extent has the anthropogenic activities impacted the groundwater system. Water resource managers and decision makers need this information for efficient catchments water resource planning and management.

This investigation focused on the pollution of surface water, specifically, in the groundwater management and the occurrences of pollution from municipal waste water, industries and agriculture. The scope of this study covered the types and sources of pollution as well as their impact on groundwater resources in the area of investigation. The primary objectives were (i) to determine the connectivity between groundwater and surface water, and (ii) to determine the source of pollution by anthropogenic activities in groundwater systems.

According to BRS (2006), the following hydrogeological parameters are useful when evaluating groundwater and surface water connectivity: groundwater availability (borehole yield), groundwater quality, groundwater flow paths, aquifer hydraulic properties (transmissivity and storativity), and aquifer structure (normally aquifer boundaries, structural contours of the aquifer both top and base, aquifer thickness, and specific features such as faults).

1.3 Problem statement

The chemistry of groundwater and surface water resources in the Uitenhage area are less understood; the lack of information on these components has been of a concern. The existing literature showed that for the past decades, the water pollution of the Swartkops River has raised many concerns to the community in the area (Binning and Baird, 2001). Amongst those concerns from the Swartkops River are that it has not received much attention and it poses a threat to the water users. The most obvious polluting activities are the domestic waste (sewage) and wastewater from industries. Therefore, the main concern is that, there is no monitoring of compliance from the industries and discharge from municipality. However, the Water Quality Management Plan was documented and the monitoring has been neglected. There is no knowledge to what extent the impact of pollution has propagated into the groundwater system. This issue can, in a long term, result in a complete contamination of the Uitenhage Artesian Aquifer because of the contaminants source from the river as indicated by Maclear (1993) and Robert (2013). According to Binning and Baird (2001), the concentration of pollutants in water can be low and discharge level of contaminants meet the water quality criteria, however, the levels maybe elevated in the sediment and in a long-term can accumulate and cause high loads of pollutants. Therefore, understanding the chemistry of groundwater and surface water resources can close the gap.

1.4 Research questions

1. Is groundwater connected with surface water in the area and what are the sources of water that feed the springs?
2. Do the existing WWTWs and industries in the study area have any impact on water resources, if not, what are other sources of pollution?

1.5 Aim and objectives

1.5.1 Aim of the study

The study aims to establish an understanding of groundwater and surface water interactions of the TMG aquifers in Uitenhage area using environmental isotopes (stable isotopes of oxygen and hydrogen, and radioactive isotopes of tritium), hydrochemistry and faecal coliform bacteria.

1.5.2 Objectives

The objectives of the study were:

- To establish the relationship between surface topography and groundwater level elevation by using Bayesian Interpolation method and to determine the groundwater flow direction using surfer 8 software.
- To establish groundwater and surface water interaction in the study area using environmental isotope analysis, hydrochemical analysis, trace metals, bacteriological analysis and to develop a site specific conceptual model to illustrate the connectivity between groundwater and surface water.

1.6 Structure of the Thesis

Chapter one: Gives the general overview, introduction, which introduces the research topic, the problem statement that has triggered to the study.

Chapter two: Provide the general overview of the study area such as sampling site, physiography, climate, land use, geological setting and hydrogeology of the area.

Chapter Three: Describes the approach and gives the fundamental concepts that assist in general understanding of the groundwater and surface water components.

Chapter four: Gives the discussion of the list of methods that have been used in the study.

Chapter five: Discusses the outcome of Bayesian Interpolation Method, which was used to establish the relationship between surface topography and groundwater level elevation. It also gives more information about the groundwater flow direction in the study area.

Chapter six: It gives the overview of the use of the environmental isotopes analysis, hydrochemical analysis including trace metal as well as biological analysis.

Chapter seven: It summaries the conclusion of the results as well as the recommendation where suggestions are made on what should be done in the next investigation.

2. CHAPTER TWO: STUDY AREA

This chapter provides the description of the study area, data collection sites.

2.1 Introduction

The Uitenhage Aquifer Basin (UAB) is the main groundwater supply in the Uitenhage area, which supplies water from the springs for large agricultural irrigation schemes, domestic and industrial water use. The eastern part of the Uitenhage Artesian Aquifer (UAA) comprises of the Cretaceous siltstones and mudstones underlined by the confined fractured Table Mountain Group (TMG) sandstone that generated the artesian conditions (Maclear, 2001).

The study area is located around the Uitenhage town, Eastern Cape Province of South Africa. It falls within Mzimvubu to Tsitsikama - Water Management Area (WMA 7). It covers the following quaternary regions: M30A, M30B, M10A, M10B, M10C and M10D and is sub-divided into two sub-catchments, which are Coega River catchment and Swartkops River catchment. The total catchment area is 1938 km^2 (Figure 1). The Coega River catchment is located in the northern part and covers an area of 515 km^2. In the Coega River catchment, there is an artesian aquifer which consists of imperative springs, located in the northern part of the Uitenhage town. These springs are artesian in nature due to the underlying geological configuration. The community as well as irrigation schemes of the Uitenhage area are largely dependent on these springs and they have been regarded as the main water supply source since the 1800's (Venables, 1985). The Swartkops River catchment is located in the southern part and covers the area of 1423 km^2. The Swartkops River catchment covers almost the entire municipal area of Uitenhage, Kwanobuhle, Despatch, Ibhayi/Algoa and also half of the Port Elizabeth municipal area (Binning and Baird, 2001). The Swartkops River is an important source of freshwater ecosystem in catchment (Taljaard *et al*. 1998). It is the only large perennial river in the Uitenhage area that is assumed to have interconnection with the underlying aquifers. The Swartkops River catchment is impacted by high housing density that has been developed in the catchment and an increase in contamination from industries of Uitenhage (Binning and Baird, 2001).

2.1.1 Description of the study area

2.1.1.1 Sampling sites

The sampling sites (Figure 1) were selected along the Swartkops River and they consist of three sampling points: i.e. upstream (S1), midstream (S2) and downstream (S3). The S1 point was selected as a control which has no anthropogenic influences. The Uitenhage comprised of a number of industries which are continuously discharging pollutants to Swartkops River. In addition to industries, municipality also contributes with the discharge of wastewater directly into the river. The S2 point (Figure 2 and Figure 3) was selected as entry point of the water pollutants. The S3 point (Figure 4) measures the concentration of the pollutants that may have dissolved in water from the midstream point and intermediate catchment.

Hydrocensus was conducted to identify production boreholes around the study area in order to determine the extent of pollutants that may have infiltrated into groundwater systems. Six production boreholes including the Uitenhage spring are found in the close proximity of the study area and are shown in Figure 1. The closer view of the Uitenhage Spring and some of boreholes is shown in Figure 5, Figure 6 and Figure 7.

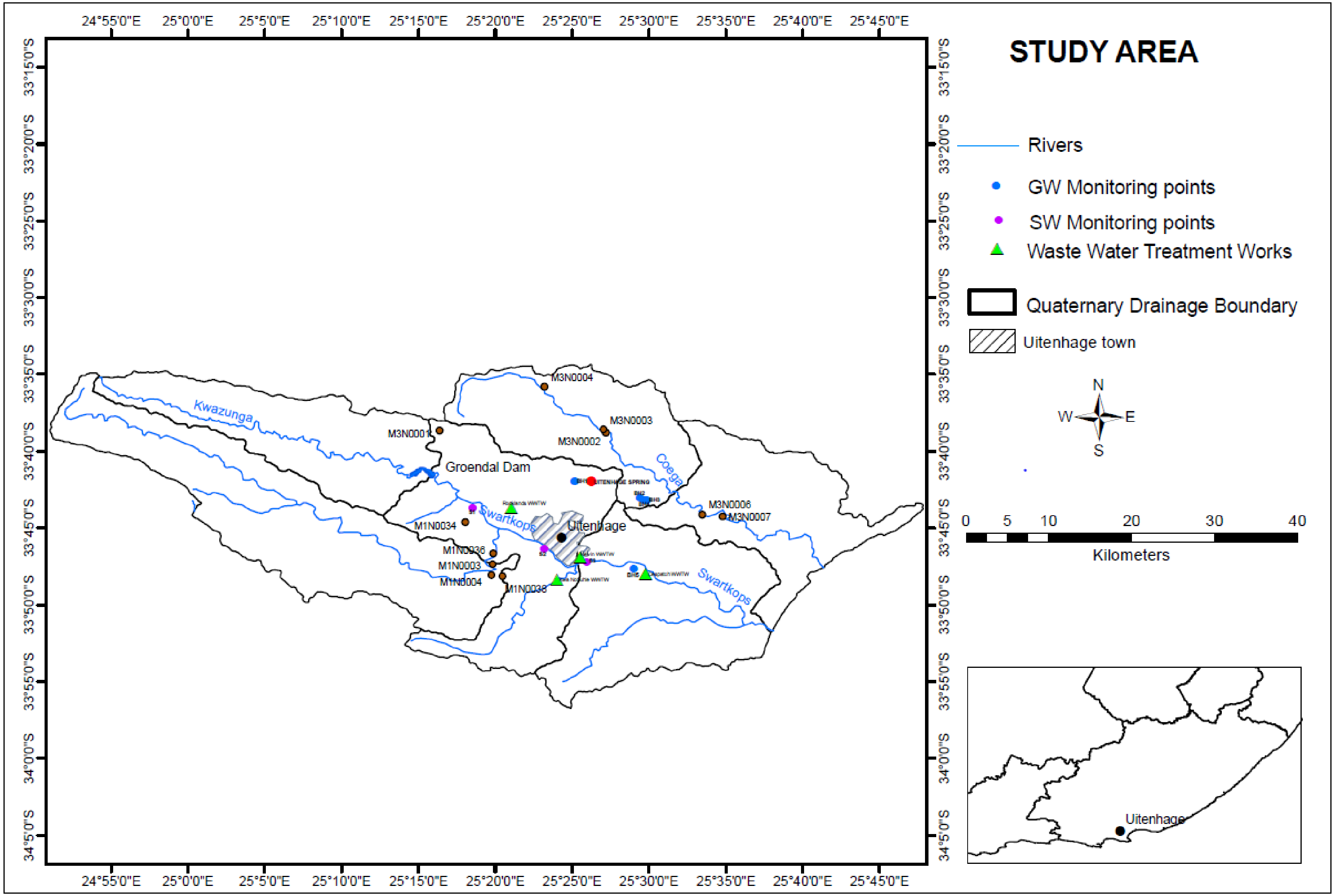

Figure 1: The location of the study area in relation to the Eastern Cape Province

Figure 2: S2 (Swartkops River-midstream point), during the high flows in November 2015.

Figure 3: S2 (Swartkops River- midstream point), during the low flows in January 2016.

Figure 4: S3 (Swartkops River- downstream point).

Figure 5: Uitenhage Spring.

Figure 6: Borehole at No. 287 Doorenkom farm (BH1).

Figure 7: Borehole at Sovereign foods (BH3).

2.1.1.2 Physiography

The study area has two major rivers: the Swartkops River and Coega River. The Swartkops River forms the southern boundary of the study area and extend towards southeast (Figure 8) where the flow is towards the Indian Ocean through the Blue Water Bay, north-east of Port Elizabeth. The Swartkops River has two main tributaries *viz:* north western Kwazunga and western Elands River. The other small ephemeral tributaries are the Sand, Brak and Chatty River, which drain the south-eastern parts of the catchment area (Figure 8). The northern boundary is Coega River, which drains eastwards from the Groot Winterhoek Mountains to the sea.

The western side of the study area is bounded by the Groot Winterhoek, Elands and Zunga Mountains, which stretch towards the south, in the low-lying Van Stadens Mountain (Marais, 1964; Maclear, 2001). The Van Stadens Mountain is the main recharge area of the Coega Artesian System (Venables, 1985). The eastern and south-eastern reaches are characterised by mountain ranges fringed by low-lying areas (Venables, 1985; Maclear, 2001), (Figure 8).

The Uitenhage springs lie within the boundaries of fractured TMG aquifer at the foot of Groot Winterhoek Mountain (Figure 8). The Uitenhage Artesian Aquifer (UAA) is one of the well-known artesian aquifers in South Africa and the springs are found mostly in the north western parts of town of Uitenhage.

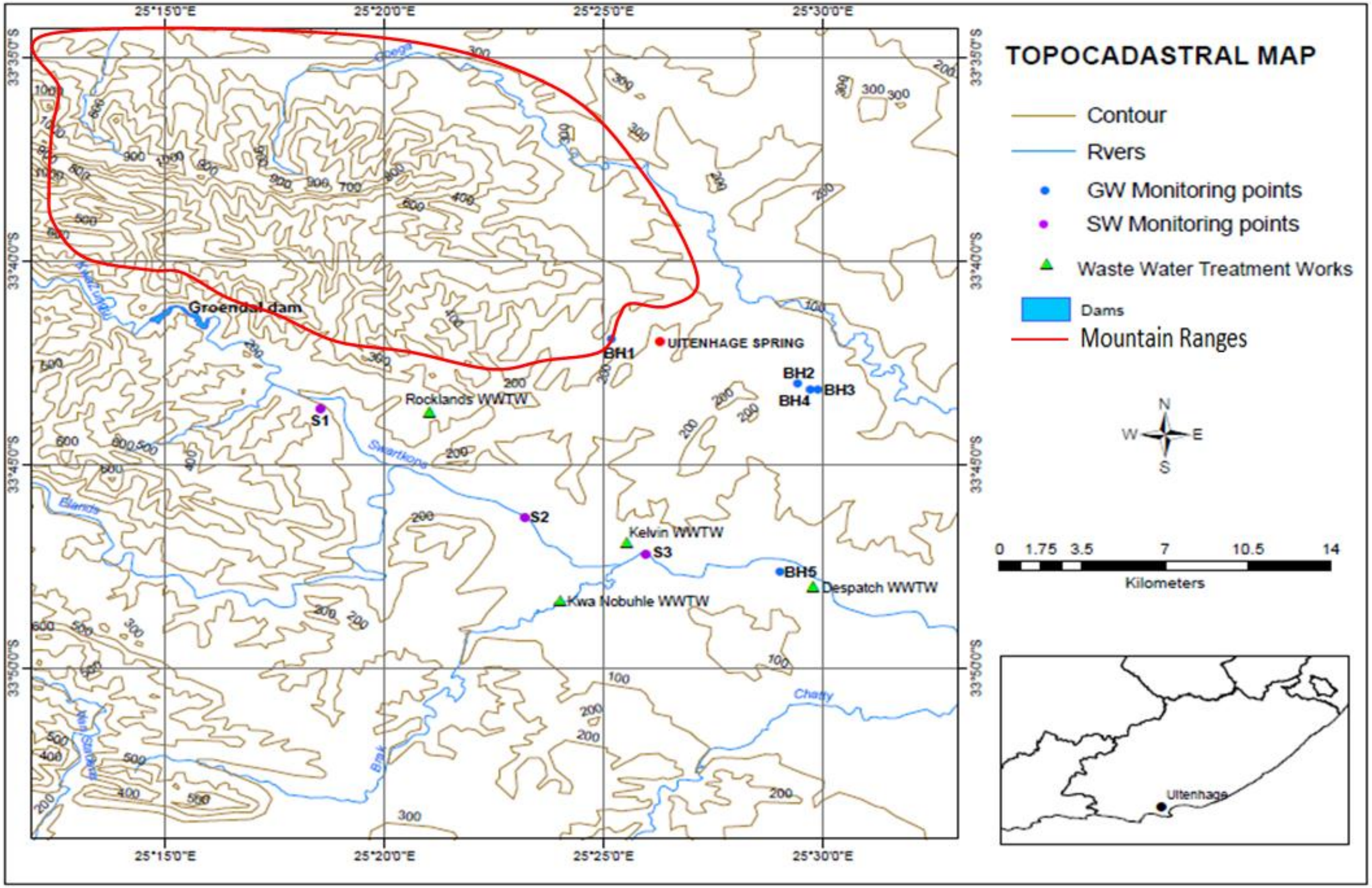

Figure 8: The elevation of the study area.

2.1.1.3 Land-use

Figure 9 shows the landuse and land cover of the study area which forms part of the Nelson Mandela Bay Metropolitan Municipality. The vegetation cover is mainly thick bush (thicket, bushland bush clumps and high fynbos) with patches of grasslands (shrubs and low fynbos). The sand mining areas occur in the i) western part of Uitenhage town along the KwaZunga River (upper tributary of Swarkops River), ii) along Swartkops River west of Uitenhage town, iii) north eastern part of Uitenhage, and iv) east and west of the Despatch. In addition to the sand mining activities west of Uitenhage the area comprises of rock outcrop that is mainly for aquifer recharge.

The study area consists of several Waste Water Treatment Works that are assumed to have a major impact on the Swartkops River water quality. While livestock farming and cultivation occurs upstream of the Uitenhage town along the Swartkops River and Elands River, some small scale farming activities occur downstream of the Uitenhage town. The north-eastern part of the town, along the Coega River, has some forest plantations. The Groendal Dam (Figure 9), which is located in the upper reaches of the Swartkops River catchment is a source of water supply for irrigation. However, some farms in the areas are dependent on groundwater for irrigation water use. The intensive irrigation mainly occurs in the Kruis River area; Kruis River is a tributary of the Elands River.

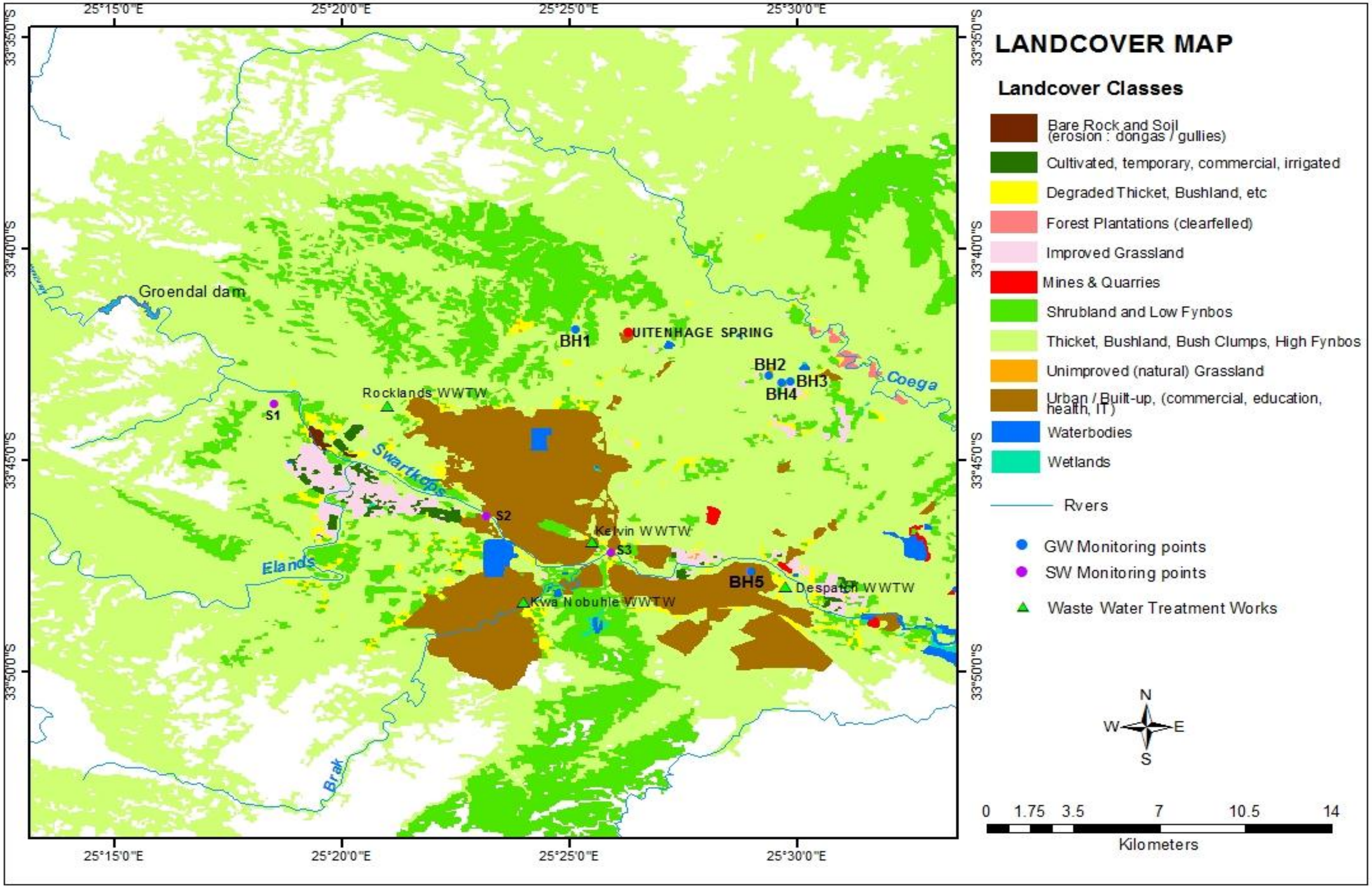

Figure 9: Map showing landuse and land cover of the study area.

2.1.1.4 Climate

The study area experiences high rainfall in the western part during winter and summer season. The climate in the area is generally hot in summers and mild to cool in winters. The eastern part of the catchment is humid and receives more rainfall than the downstream parts. While the study area receives rainfall throughout the year (Figure 10), generally, the mean annual rainfall in the area is 523 mm. The highest monthly average rainfall is received in October (73.9 mm) and lowest monthly average rainfall is received in May (21.2 mm) (Figure 10). Average daily temperatures at the Uitenhage area range between 19.8°C in July to 26.9°C in February (Schultz, 1997).

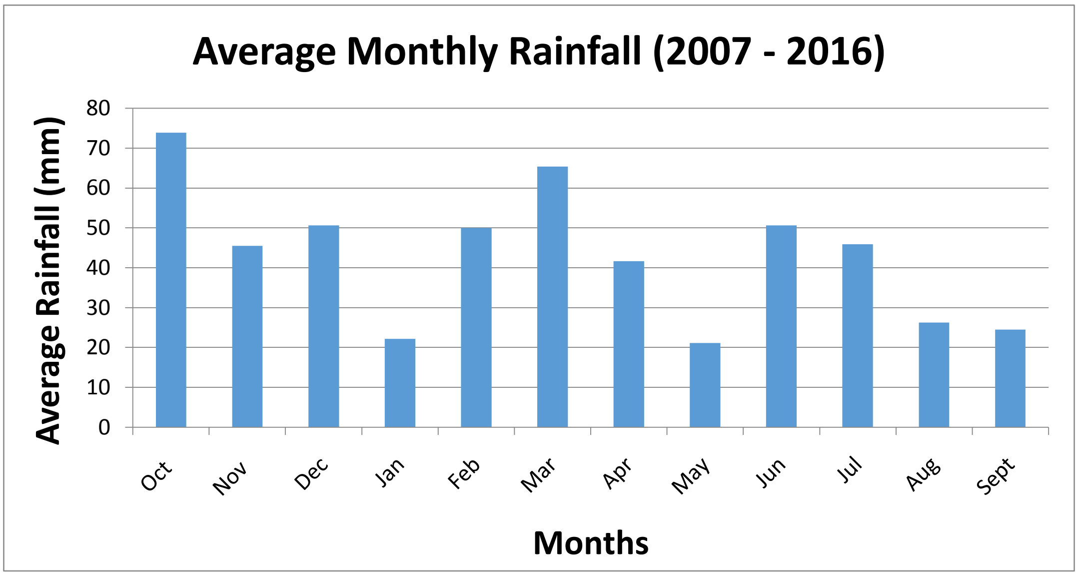

Figure 10: Monthly rainfall data collected from the period 2007 to 2016 at station M1R001.

2.1.1.5 Geological setting

The western part of the Swartkops River catchment consists of the Groot Winterhoek Mountain and Kwazunga River valley, whilst the Elands and Van Stadens Mountain lies on the southern part (Figure 11). The Groot Winterhoek Mountain and Kwazunga River valley are characterized by the quartzitic sandstone of the TMG (Maclear, 1993, 2001). The Elands River sub-basin, which forms part of the Swartkops River catchment consists of sandstones and black shales of the Ceres Formation (Toerien, 1989) and the central part comprises, predominantly of alluvium deposits in the valleys and floodplains (Maclear, 1993). The eastern part of the Uitenhage basin is characterised mainly by Kirkwood, Quaternary and Sundays River Formation and some patches of the Alexander and Bluewater Bay Formation; whereas the northern part consists of predominantly of the Kirkwood and Sundays River Formation.

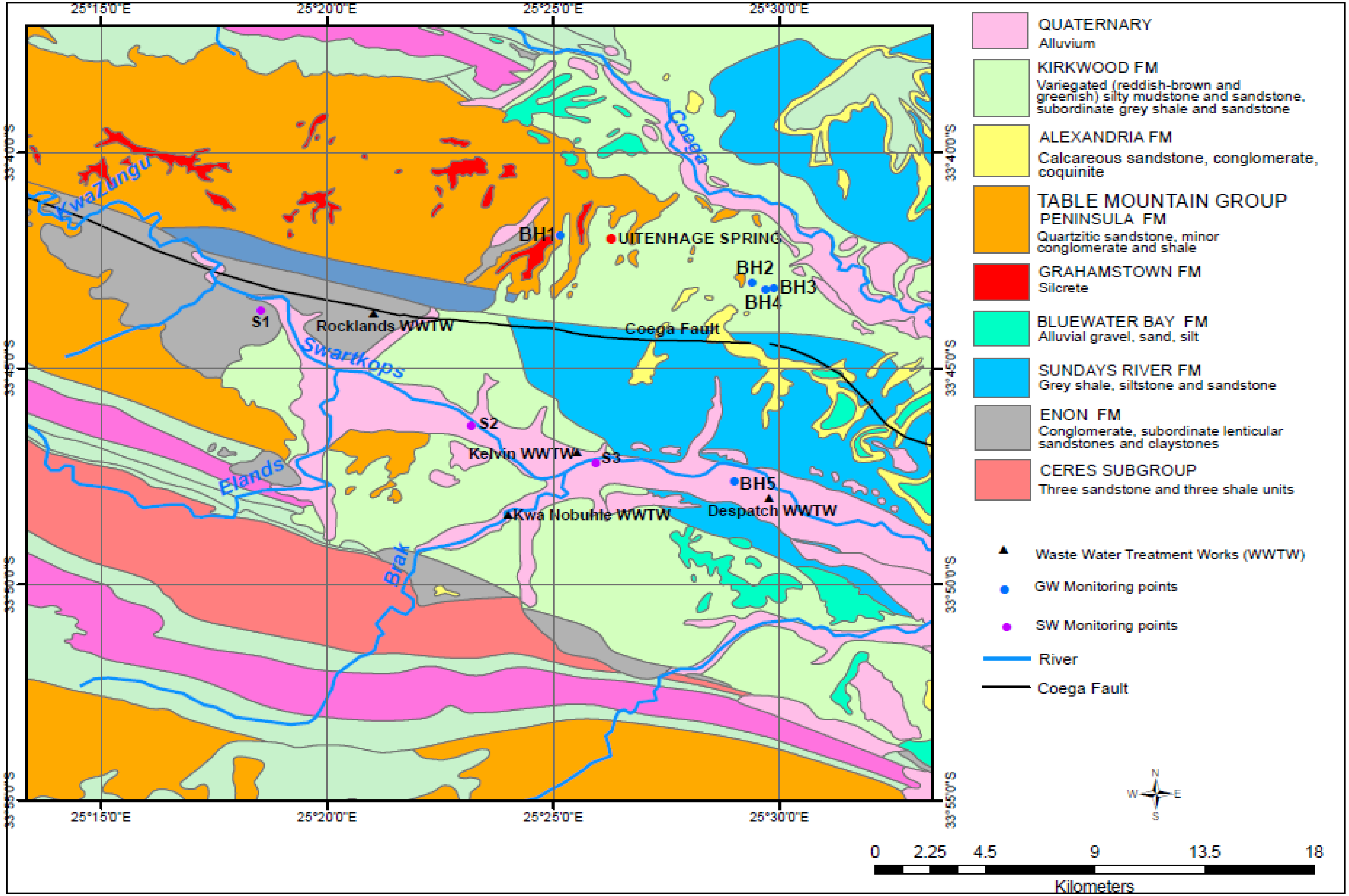

Figure 11: The main geological formation of the study area.

Table 1 presents the lithologies of both production and monitoring boreholes used for investigation in this study. The Doorenkom farm production borehole (BH1) was drilled (Figure 11) on the TMG with a depth of ±100m and depth of the pump was at 93 m. The Uitenhage spring is at the edge of the TMG on the Uitenhage group as well as three production boreholes, *viz*: Amanzi 3 (BH2: artesian well), Sovereign foods (BH3) and Sovereign foods at Rietheuwel (BH4).

Table 1: The geological groups, subgroups, formations and thickness (Kent, 1980)**.**

Group	Subgroups	Formation	Thickness (m)
TMG		Basalt Sardinia Bay formation	180
		Peninsula formation	1500
		Cedarberg formation	50
	Nardouw Subgroup		850
Uitenhage Group		Basal Econ	3000
		Kirkwood	2200
		Sundays River	1600

2.1.1.6 Hydrogeology

The Uitenhage Artesian Basin (UAB) aquifer system comprises of fractured sandstones of the TMG which are confined in the eastern part of the basin and overly the Cretaceous siltstones and mudstones, resulting in artesian conditions (Venables, 1985; Maclear, 2001). The aquifer is recharged mainly by rainfall on the Groot Winterhoek and Kwazunga Mountains (Maclear, 2001). The Cretaceous siltstones are weathered and intensively fractured with high capability to store water. They constitute important aquifer and their permeability is controlled by the stress of the regional pattern of the TMG aquifer. The TMG aquifer system is a regional aquifer, which is regarded as a main water source for future supply in both the Western and Eastern Cape Provinces. The TMG Aquifer (Figure 11) consists mainly of metasandstone (sometimes identified as quartzitic sandstone), minor conglomerate and shale; the quartzites are exploited extensively for agricultural purposes. This aquifer occurs at significant depth and is protected by an aquiclude that is important for the formation of springs and shallow aquifers. It is important to note, however, that this aquifer needs to be protected because of its high yield and good water quality. The quartzitic sandstone of the TMG are overlain by thick post-Palaeozoic sediments giving rise to an artesian groundwater flow conditions. The other side of the Coega Fault, at the western part of the study area, consists of the confined TMG outcrop, which is also a source of aquifer recharge. In the Algoa Bay, there are three small islands consisting of the sediments of the TMG. These sediments comprise of quartz with minor conglomerate and mudstone beds (Venables, 1985).

The lithology of the Enon Formation consists of conglomerates, subordinates lenticular sandstones and clay stones. However, it does not have a significant hydrological importance in the study area, it occurs in a small portion to the west and it is confined. The Kirkwood Formation relatively covers almost the entire portion of the north, east and southern part of the study area. Its lithology (Appendix B) consists of reddish brown and greenish clay, siltstone, sandstones and subordinates of grey shale, which act as an aquiclude (Maclear, 2001). The Sunday's River Formation outcrop occurs in the north eastern part of the spring and more at the southern part of the Coega fault (Figure 11). However, these three formations viz: Enon, Kirkwood and Sundays River are grouped as Uitenhage Group (Venables, 1985).

Figure 12 shows that the study area comprises of two imperative aquifers, which are separated by Coega Fault, i.e. the shallow unconfined primary aquifer (Coega Aquifer) to semi-confined and relatively deep secondary artesian aquifer (Swartkops Aquifer) (Maclear, 1996; Maclear, 2001).

Figure 13, Figure 14 and Figure 15 illustrate the cross section of Coega (B) and Swartkops (C) aquifers as well as the diagonal cross section of both aquifers. These figures also show rivers, faults and borehole depths relative to the underlying geological formations.

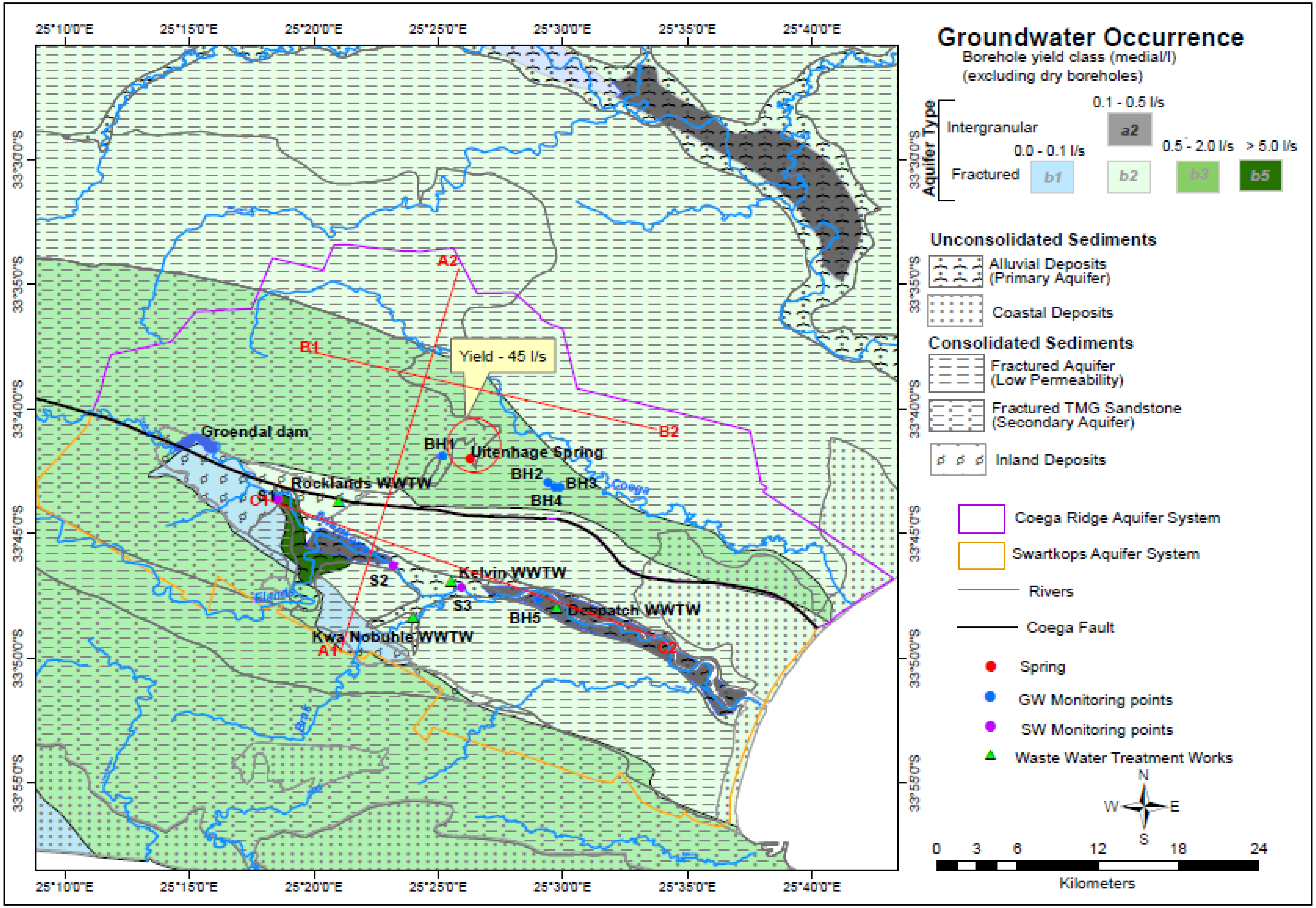

Figure 12: The hydrogeology of the study area.

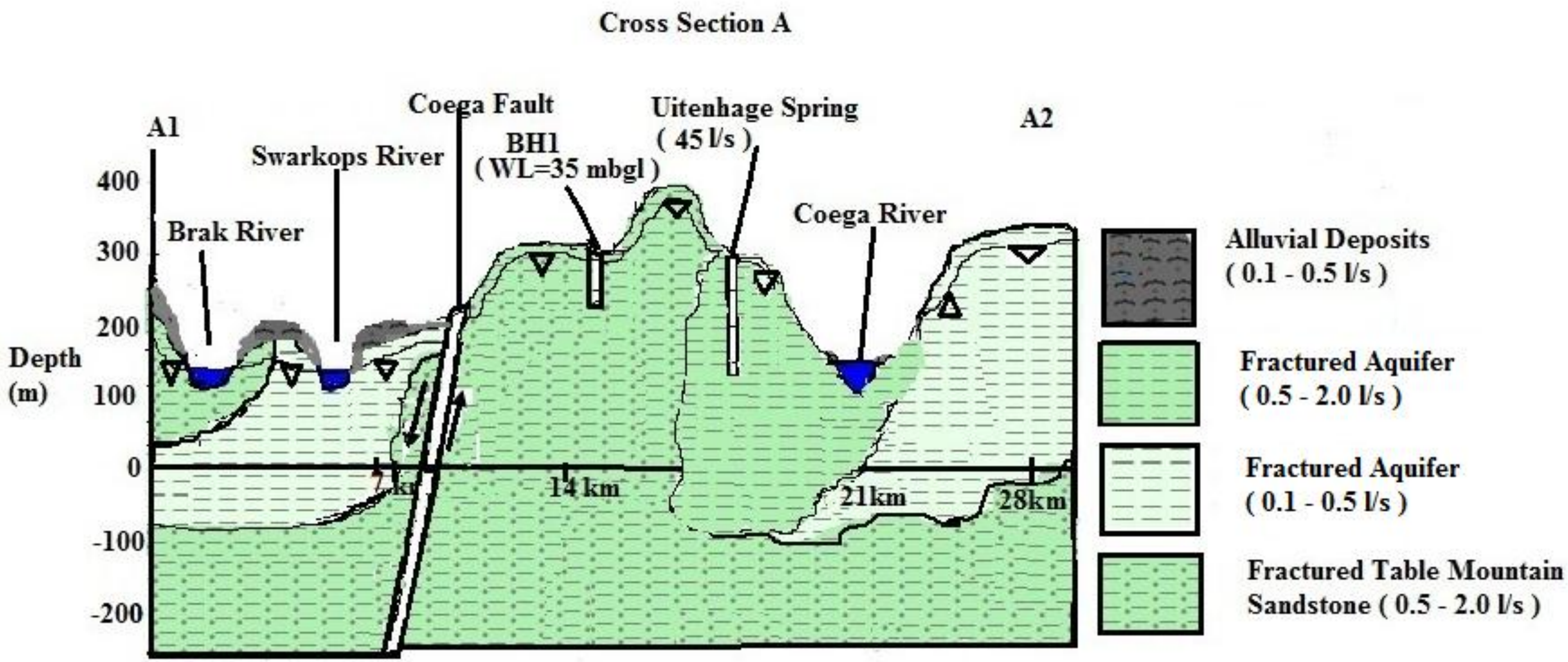

Figure 13: Aquifer cross section A (adopted from Maclear, 2001).

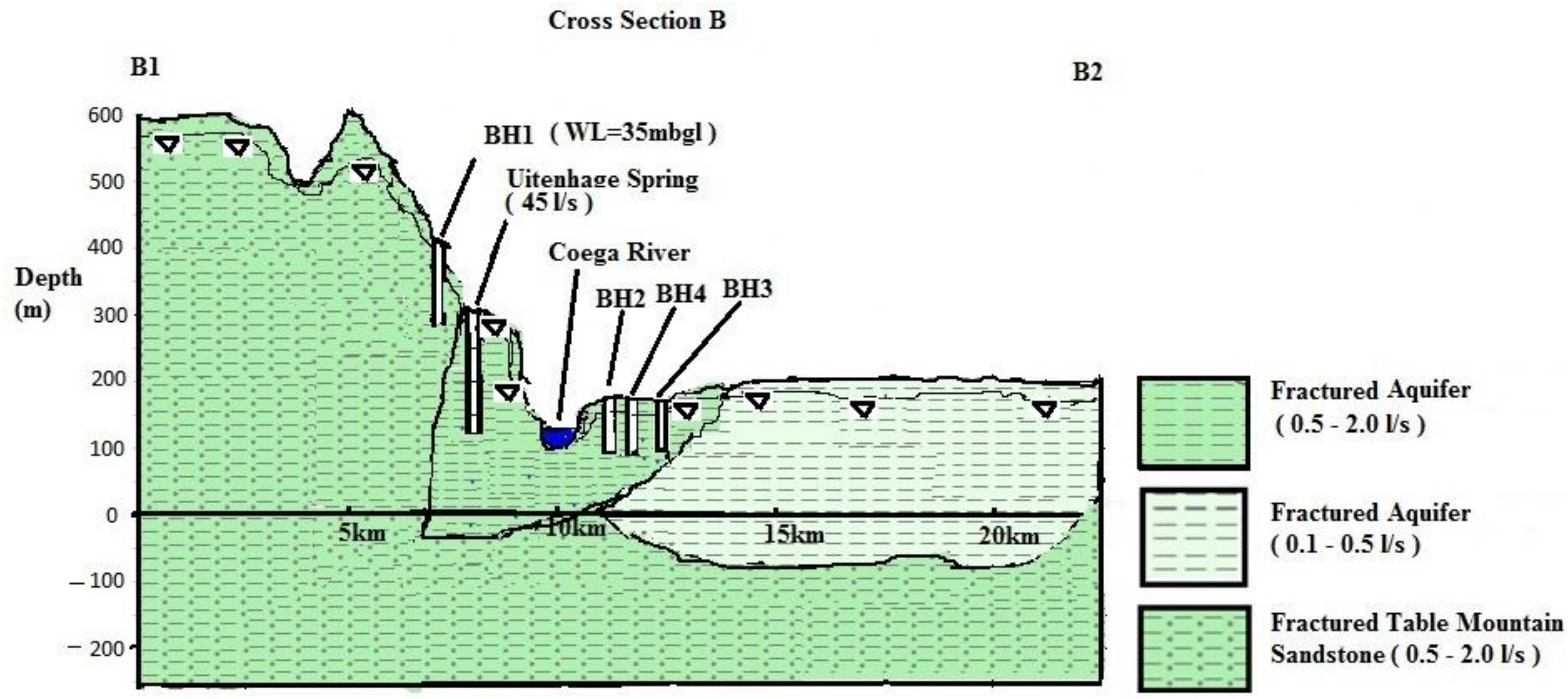

Figure 14: Aquifer cross section B (adopted from Maclear, 2001).

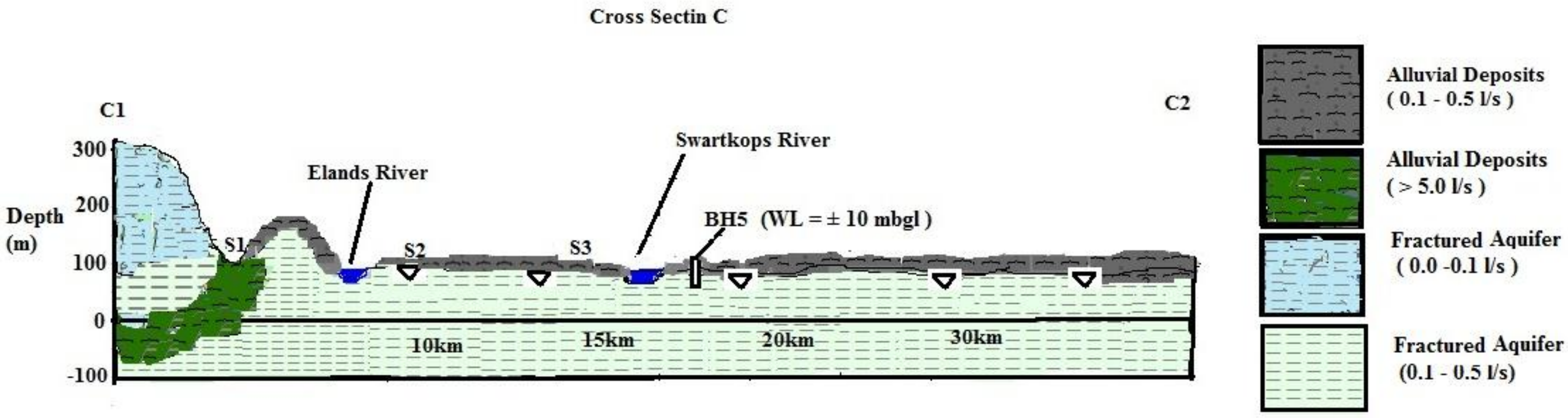

Figure 15: Aquifer cross section C (adopted from Maclear, 2001).

2.1.1.7 Coega Ridge Aquifer (CRA)

The Coaga Ridge Aquifer (CRA) stretches from the western side of the springs towards the eastern side (coastal). It occurs at the northern portion of the Coega fault at relatively shallow depth (Maclear, 1996; Maclear, 2001). The Uitenhage Group of the aquifer consists of impermeable mudstone and siltstone, which are found in the eastern part of the spring. These impermeable layers overlie the quartzite of the TMG, which forms an aquiclude. The aquifer stretches towards the coast, in the easterly direction. The aquifer is a primary source for economical large scale abstraction of groundwater; as a result, groundwater is used for irrigation of citrus fruit and lucerne, as well as domestic use (Maclear, 2001).

Uitenhage Spring

The Uitenhage area has numerous springs that are well known in South Africa. They are derived from an artesian basin and used for water supply to the Nelson Mandela Bay Metropolitan Municipality. The springs are used for domestic water supply as well as irrigation schemes; they are found in the Coega Ridge Aquifer and are supplied by the unconfined part of the TMG aquifer system. The Uitenhage springs are at the edge of the TMG outcrop (mountain) and are fault controlled (Figure 13). The springs (eyes) are nine in total with combined flow of 45l/s, according to Xu and Maclear, (2003).

2.1.1.8 Swartkops Aquifer

The Swartkops River Alluvial Aquifer is a thin layer, which stretches to the south of the Coega Fault (Maclear, 2001). It further stretches from Groendal Dam, at Kwazunga Mountains, down to east of Port Elizabeth. The hydrogeological conditions of the aquifer are similar to that of CRA; however, the Swartkops Aquifer occurs at a greater depth of the TMG aquifer in relation to Coega Ridge Aquifer, approximate 100 m to 120 m deep towards east direction (Maclear, 1996).

3. CHAPTER THREE: LITERATURE REVIEW

3.1 An Overview:

Groundwater always flow from higher hydraulic gradient to lower hydraulic gradient area, which means an increase of the elevation of the surface will also increase the groundwater hydraulic gradient, where it discharges into the rivers (streams), lakes, dams and springs (du Plessis, 2010) as a base flow and get stored in rock interstices. Surface water features, generally, interact with groundwater features (Winter *et al*. 1998), which means the impact of the other can have a significant effect to the other in terms of both quality and quantity. Previously, surface water and groundwater resources were managed as individual entities. This has a significant effect in the planning and management of water resource, such as water allocation, i.e. the water parcel that has been allocated, can also be allocated more than once to groundwater users as well as to surface water users. Therefore, this overlap can cause serious problems where one water resource is over allocated (Annan, 2006).

According to Wright (1980), "abstraction from surface water and groundwater for supply purposes are limited by both quantity and quality considerations. When there is a flow of water between the surface and aquifers, in either direction, there is a relationship between the qualities of water in the two systems".

The water resources optimum management requires a bigger picture about the connectivity of groundwater and surface water systems, which is also an important factor of the hydrological cycle (Robert, 2013). Over the past years, the main focus has been on studying and understanding the interconnection between groundwater with rivers and lakes as these are the dominant entrance and exit points of surface and sub-surface interaction that are critical in terms of water resource management (Sophocleous, 2002; Yang *et al*. 2012). However, the emphasis on the strategy of managing water resources requires a comprehensive investigation and thorough understanding of the interconnections between these two resource components, particularly, in case of pollution (Egboka *et al*. 1989). Understanding the interaction between these components has not received scientific attention especially in water management sector (Winter *et al*. 1998). Therefore, it is imperative to understand their connections for planning and water resource management purpose, as well as protection and pollution control thereof.

The available techniques for the determination of groundwater and surface water interconnection are broad; therefore, a method has to be chosen based on the purpose of the study (Kalbus *et al*. 2006). The interconnection between these two components have been investigated using several methods, for example, tracer tests (Ptak *et al*. 2004), time-series temperature measurements (Stonestrom and Constanz, 2003), heat tracer (Kalbus *et al*. 2006), mass balance approaches (Kalbus *et al*. 2006), environmental tracer methods (Crandall *et al*. 1999; Herczeg *et al*. 2001; Baskaran *et al*. 2004; Abiye, 2013) as well as microbiological method (bacteriological assessment or bacterial culture) (Bordner, *et al*. 1978). Amongst the above-listed methods, the environmental tracer method (isotopes and hydrochemistry) and bacteriological assessment (Bacterial Culture) have proven to be useful in understanding the interconnection between groundwater and surface water (Abiye, 2013; Suarez *et al*. 2015) and are mainly used in the current investigations. While these two methods are the most effective, they however, have their own advantages and disadvantages. Therefore, it is so imperative when selecting the method to be applied in the case study area, to first consider the study aim and objectives. The above selected methods (environmental tracer and faecal coliform bacteria) have following advantages: they are relatively easy to apply and cost effective, and they are commonly employed in investigating the interconnection between groundwater and surface water (Abiye, 2013; Suarez *et al*. 2015). The selected methods are described in more details in the sub-sections below.

3.1.1 Environmental Tracer Method

Environmental isotope studies provide important information on the source from which the water derived for management purpose and are also useful tools in the effective management and water resource analysis at different spatial scale both at local and catchment level (Abiye, 2013). The application of isotopes is essential in the identification of the sources of groundwater and pathways in different aquifers (Sophocleous, 2002; Kalbus *et al*. 2006,). They provide distinctive information on water resources connectivity and transport (Clark and Fritz, 1997; Abiye, 2013).

The environmental tracer methods such as hydrochemistry, stable isotopes (^{18}O and ^{2}H), and radioactive isotopes of tritium or carbon are naturally-occurring dissolved constituents mainly used in the determination of groundwater movement (Cook, 2003). The most commonly used field parameters in environmental tracers include electrical conductivity (EC), pH, dissolved oxygen, temperature, major ions of calcium, magnesium and sodium, stable isotopes, and radioactive isotopes (Brodie *et al*. 2005).

The environmental isotope method was successfully established in the Isotope Hydrology Section – Vienna in 1959. After some experimental studies, the United States of America, Canada and Germany successfully demonstrated the possible use of the environmental isotopes as natural tracers of water (Taylor, 1976). The environmental isotope method was sufficiently advanced in the early years of 1960s to be applied in the field (Taylor, 1976). In 1966, the use of environmental isotopes had become significant in the groundwater hydrology investigations. Therefore, most of the studies then started to make use of environmental isotopes or artificial tracers in their investigations, especially in the developing countries (Taylor, 1976).

Isotopic methods and hydrochemistry were selected for establishing the groundwater and surface water interaction for the study area. The results will provide critical information about hydrological processes, such as the interaction of river water, groundwater as well as spring water.

3.1.1.1 Stable Isotopes

Oxygen and Hydrogen

Stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H or D) are essential tool for tracing the recharge, history, and contamination of groundwater (Clark and Fritz, 1997; Abiye, 2013). Stable isotopes of ^{2}H and ^{18}O are commonly used in groundwater and surface water interaction since surface water is more enriched in ^{2}H and ^{18}O compared to groundwater (Yehdeghoa *et al*. 1997; Coplen *et al*. 2000; Hinkle *et al*. 2001). These isotope ratios have been used as tracers in several studies since the 1960s (Freeze and Cherry, 2002; Clark and Fritz, 1997; Abiye, 2013).

Tritium

Tritium (^{3}H) is a radioactive isotope of hydrogen and with half-life of 12.43 years. It is a useful tool for tracing the circulation time of groundwater, particularly the recharge that occurred in 1950s and early 1960s (USGS, 1999). This is following the nuclear testing of bombs during 1950s and early 1960s. These human activities have resulted in the accumulation of the chemical pollutants and isotopic constituents of tritium into the atmosphere. Therefore, chemical constituents from the atmosphere have mixed and spread all over the world. As a result, tritium dissolved in rainwater and became available in the hydrologic cycle. Therefore, these chemical constituents of tritium can indicate the source (stream, aquifer, etc.) from which the water is derived (USGS, 1999).

3.1.1.2 Hydrochemistry

The understanding of hydrochemistry is important in determining the origin of groundwater (Zaporozec, 1972). Analysis of the chemical constituents and their interpretation in the water samples can indicate the source (e.g. stream or an aquifer) from which the water is derived. The groundwater chemical composition is controlled by various factors such as precipitation, lithology, climate, topography, and anthropogenic activities (e.g. agriculture, industries) (El Kashouty, 2013). The natural occurring dissolved constituents can be used to trace the groundwater movement such as heavy metals (e.g. copper, lead, and cadmium) and major ions of calcium, magnesium and chloride (Cook, 2003).

Metals are toxic and are detrimental to human health. They are naturally occurring in the soil and can be as a result of geological processes (Radwan and Salama, 2006; Duran *et al*. 2007; Tuzen and Soylak, 2007), anthropogenic activities such as municipal wastes (sewage), agriculture (fertilizers), mining and industries (burning of fossil fuels and smelting of metal like ores), which carry large amount of metals that are released to the environment (Nriagu, 1979; Pendias and Pendias, 1989; Rai, 2009). According to Concas *et al*. (2006) and Rai (2008), the contamination from metals including acid mine drainage are the main concerns to the environment.

According to Kamran *et al*. (2013), soils contain the following average levels of metals: Aluminium (Al), Lead (Pb), Zinc (Zn), Cadmium (Cd), Manganese (Mn), and Copper (Cu) are 66200.0, 0.097, 22.6, 583.0, 26.0 and 74.2 mg/kg, respectively. However, high level of metals in soil can eventually have impact on plants, animals and humans when transferred through food chain.

Cadmium and lead are most common heavy metals which are particularly toxic and poisonous; the excessive amount in food can cause diseases in kidneys, nervous systems and bones (Kamran *et al*., 2013).

3.1.2 Bacterial Culture

Globally, human activities have proved to be the main cause of water pollution in many rivers as compared to the natural changes in the water quality (Makela and Meybeck, 1996). The urban settlements and municipalities produce nutrients from sewage effluent, industries (toxic substances) and fertilisers (nitrates) which can affect both groundwater and surface water quality (Dhiviyaa *et al*. 2011). It has become a phenomenon that fresh water resources are affected by chemical, microbiological and thermal pollution (Bertsch, 2010). Worldwide, the linkage between the groundwater and surface water has shown to be a major concern and understanding their interaction is essential to water managers and scientists at large (Winter, 1998). Mainly in case of contamination it is essential to understand their processes as well as the protection of water resources (Kalbus *et al*. 2006).

Pathogens are microorganisms that generally cause diseases in drinking water and can be categorised in different sizes such as, bacteria and viruses, which can range from 0.5 to 1.0 µm and from 0.01 to 0.1 µm, respectively (Uwimpuhwe, 2012). The microbial of faecal origin can be transferred to drinking water and pose a serious threat, which includes *Salmonella Typhi*, *Shigella spp*, and *Escherichia Coli* (*E. Coli*). Microorganisms such as an *E. Coli* can accumulate in sediments and mobilized with the fluctuations of water flow. Hence bacterial pathogens will likely disperse extensively and quickly (WHO, 1999; UNICEF, 2008).

The group of faecal coliforms includes other organisms such as Enterobacter group, which originates from non-faecal sources and *E. Coli* that is originating from birds and warm blooded animals. The presence of total coliforms in samples of water can indicate the presence of bacteria such as Enterobacter (pathogenic *E. Coli*, pathogens of Shigella, and Salmonella) which can multiply in water environment (Uwimpuhwe, 2012). The availability of these organisms can results in diseases such as salmonellosis, cholera, gastroenteritis and typhoid fever (DWAF, 1996; WHO, 2003). Most of the *E. Coli* are harmless, however, others can result to various infections and diseases such as diarrhoea, urinary infections, respiratory diseases as well as other diseases (Potgieter, 2007).

Enterobacter Aerogenes is a gram negative bacterium, it can be found in marine and freshwater, sewage and soils. It can also cause infections such as respiratory and urinary infections. Enterobacter is usually present in many healthy vertebrates (Langley, *et. al*. 2001). In addition, it also causes infections that may result to death, i.e. notorious nosocomial infections (Carbonne, *et. al*. 2013).

Detection of bacteria in a water source could indicate the presence of pathogenic organisms that are likely to be the source of waterborne diseases; the type of bacteria may also indicate the source of water that is associated with, i.e. sewage, industrial waste, agriculture etc. (Macler and Merkel, 2000). *E. Coli* causes various diseases, such as urinary tract infection, wound infection, gastrointestinal infection and Bacteraemia (Raina *et al*. 1999).

Therefore, the infiltration of surface water carrying chemical and sewage pollutants into groundwater can result to gastrointestinal infections or diseases, as faecal material may contain numerous pathogenic microbes (Schijven *et al*. 2013). Groundwater is the main water supply in the study area for agriculture, industries and domestic water use; therefore, its contaminants can result in poor drinking water quality, loss of water supply and high treatment costs.

3.1.3 Previous Studies

The review is not only limited to the previous studies that were conducted in the study area but it also covers the most recent global, regional and local studies. The main focus of this review was on environmental tracer's methods such as hydrochemistry, isotopes, and bacterial culture method. These methods are commonly used worldwide (Abiye, 2013) and they were also applied in the case study area.

3.1.3.1 International Context

Celiker (2016) conducted a study on groundwater and surface water interaction in Uluova Region, Elazig, Turkey using environmental isotopes (^{18}O ^{2}H, and ^{3}H) and hydrochemistry (chemical analyses). Water samples were collected for both hydrochemistry and isotope analyses; the samples were analysed for Oxygen-18, Deuterium, Tritium, and Chloride (Cl^{-}) besides field measurement of temperature (T) and electrical conductivity (EC). The results of environmental isotopes indicated that there were three different groups of water masses in the basin during the wet and dry seasons. The isotopes results also identified that the aquifer at Uluova is fed by daily precipitation. This was also supplemented by the tritium and EC values which indicated the characteristics of mixing waters that is returning from irrigation into the aquifers and revealed that the aquifer also fed by daily precipitation.

King *et al*. (2015) conducted the hydrochemical assessment and isotopic study at Cressbrook Creek catchment in Southeast Queensland, Australia. The aim of the study was to understand the hydrological response to flood and to identify the aquifer connectivity using isotopes in conjunction with hydrochemistry. The stable isotope results indicated that the surface water samples were the major source of recharge to the dam - catchment headwaters. The isotopes results also confirmed that "the flood generated significant recharge to the alluvium in the lower part of the catchment; particularly in areas where interactions between surface water and groundwater were identified and where diffuse aquifer recharge is normally limited by a thick (approximately 10 m) and relatively impermeable unsaturated zone". Interactions were identified in several sites supported by hydrochemical assessment between the bedrock aquifers and the alluvium.

In Ijebu-Ode, Southwestern Nigeria, Bello (2013) also conducted a study to investigate the bacteriological and physicochemical qualities of water samples in the well and boreholes. Based on the results of the water samples from boreholes, a zero faecal coliform count was observed, and samples from the well water the range of counts were from zero to 4.1 x 10^2 cfu/ml. The conclusion made was that, not all the waters from borehole are safe for consumption before treated and present in well waters.

The hydrochemistry and isotope study was conducted in the semi-arid to arid region of Namibia by Miller *et al* (2013). The samples were analysed for anions and cations including EC, pH and temperature. Only the selected samples were analysed for O, H, DIC, Sr, N and isotopes of ^{14}C for dating and isotope of S. The concentrations of cations and anions including the EC and water temperature from boreholes indicated approximately 3 or 4 different water types within the region. The study illustrated that the dominant water types were Mg-bicarbonate and Na-K-mixed water type. The comparison of the results for different types of water from the known water table depths indicated that there are different aquifers in the area. The results of the hydrochemical analyses were further supported by analysis of Sr isotope in the groundwater and aquifers system, which “indicated at least two different water types present: a high Sr-concentration and low $^{87}Sr/^{86}Sr$ isotope water and a low Sr-concentration and high $^{87}Sr/^{86}Sr$ isotope ratio water”. The data of the stable isotope collected in 2008 and 2009 indicated that the composition of isotope of O and H of the boreholes were more depleted in the heavy isotopes compared to average precipitation within the region. The overall analyses of data assumed that the systems of groundwater in the Namib-Naukluft region were susceptible to human activities such as contamination and over abstraction (Miller *et al*., 2013).

Yang *et al*. (2012) conducted a study on surface water and groundwater using environmental isotopes and hydrochemistry. The study was triggered by the severe contamination of Jialu River and a secondary tributary of the Huaihe River as a result of major contaminants sources of untreated or informally treated sewage waste in some cities. Groundwater systems along the river was assumed to be connected with the surface water and therefore, the study intended to investigate “temporal and spatial variations” of water chemistry that is caused by anthropogenic activities and to “characterize the relationships between surface water and groundwater” nearby rivers in the shallow Quaternary aquifer. The results of the chemical analyses revealed that the increase of the concentration of Cl^- was due to the discharge of large amount of domestic water by the nearby city (north of Zhengzhou). The maximum concentration of Nitrate and Potassium was also identified in groundwater in one of the other nearby city (Fugou County), which was caused by the use of large quantities of fertilizers in the region. Based on comparison of the results of surface water and groundwater levels, major ions and stable isotopes signatures shown that most surface water is continuously recharged by surrounding groundwater, however, it was identified that the groundwater of a transitional well in September 2010 was recharged by river water via bank infiltration.

Batisani (2012) examined the groundwater quality from domestic water supply across Botswana rural areas using hydrochemistry. The author found that the groundwater was suitable for human consumption regardless of high levels of cations. However, in some parts of the country the levels of Na^{+}, Ca^{2+}, EC and TDS were presenting increasing trends showing the need for groundwater quality monitoring in order to terminate the pollution of the boreholes.

The hydrochemical study was conducted by Maheshwari *et al*. (2011). The aim of the study was to assess the quality of both surface water (Yamuna River) and groundwater owing to industrial waste water, municipality sewage that was being discharged into the river. The groundwater is intensively used in India for industrial and agricultural purposes; however, the deterioration of the quality of water was discovered that it's due to the land use and anthropogenic activities (De Vries, 2002). The samples were collected in both winter and summer seasons. The results of the physicochemical analysis indicated that the water quality allowable for drinking and other uses. According to the analytical results, it was also shown that during winter season the water quality was suitable for domestic use.

Kipkemboi (2011) conducted bacteriological study in the Wamba Division, Samburu District in the Rift Valley Province, in Kenya. The aim of the study was aimed at determining water quality in Wamba Division of Samburu District and to assess the effectiveness of plant extracts in purifying water. For bacteriological analyses, both multiple tube fermentation and heterotrophic plate counts techniques were used, and for physiochemical analyses, standard methods were used. In the most samples, the results of qualitative bacterial determination indicated the presence of thermotolerant coliforms, Shigella and Salmonella spp. The presence of faecal coliform load was found to be higher in dry river bed wells compared to other categories of other sources of water such as rivers, dams, springs and tap water. It was assumed that the higher levels of mean conductivity in boreholes were due to long residence time that the water was in contact with minerals. The bacteriological analyses of water quality indicated that bacterial loads for most sources of water had exceeded the WHO values or guidelines for drinking water standards. The study concluded that the water from most of the sources is contaminated; as a result, need to be treated before use.

In 2010 a water quality study was conducted in Nigeria by Ekiye and Luo (2010). The aim was to analyse the state water quality in Nigeria's industrial cities. Nigeria, as a developing country, has a huge demand in various aspects of living and the development of the economy; however, it is a priority to the Nigerian government. This has resulted in an increase in industries which led to an increased discharge quantity of pollutants to the water bodies. It was noticed that Nigeria has different regulations that were implemented to protect and control the dumping of the effluent to open water bodies and it has not been effective to protect the marine environment. The results of the study indicated that both urbanization and industrialization had an impact on the water resources of the Nigerian cities. The study discovered that there were no rehabilitation and mitigation measures in place.

Gibson *et al*. (2005) conducted an isotope hydrology research on the Mackenzie River basin, which is forming contributions to programmes of the "Global Energy and Water Cycle Experiment". The isotopes of ^{18}O and ^{2}H were used. The application of isotope tracers in hydrological studies was extensively reviewed and published by Mook (2000) and one of the objectives of the study was to review the applications of the stable isotopes (^{1}H, ^{2}H, ^{16}O, ^{18}O). The study indicated that the method is commonly used in the recent Canadian hydrological studies. The research also supported the 'International Atomic Energy Agency's (IAEA) Global Network for Isotopes in Precipitation and IAEAs Coordinated Research Project on Large River Basins'. The conclusion that was drawn from past investigations in Canada was that the combination use of oxygen and hydrogen isotopes allows the distinction of variability of precipitation from evaporation effects.

3.1.3.2 South African Context

A study of groundwater and surface water interaction was conducted in the Upper Crocodile River Basin of South Africa by Abiye *et al*. (2015), using environmental isotope in the mining environment. The hydrogeology of the study area consists of fractured crystalline rocks as well as dolomitic aquifers where groundwater is abstracted for various purposes. The results of the environmental isotopes indicated that the decanting water from the mine was extensively mixed with shallow groundwater and streams. The tritium results indicated that in dolomitic areas that lie at a distance from the mine constituted unpolluted water. From the tritium results, it was also revealed that the aquifer was recharging from old water (which had long residence time), i.e. tritium concentrations were very low for water found in dolomitic areas in contrary to the water found closer to mine. The study also revealed that the stream loose water through fractures and sinkholes into dolomite aquifer nearby the mine, as a result, the interaction between groundwater and surface water was identified.

The environmental isotope and hydrochemistry study was conducted by Mengistu *et al*. (2015) to improve groundwater flow conceptualization. The study was intended to assess the origin of excess water from the pumping shaft, which is located near Stilfontein town in North West Province of South Africa. The results indicated that the water at Margaret shaft was derived from the seepage of tailings dam (Dam 5) of the mine that is nearby as well as in the upper aquifer (dolomite). The study revealed that if the pumping was going to continue at a rate that was pumping, the neighbouring shallow boreholes from the farm were going to dry up for approximately the next 10 years at time. The stable isotopes results indicated that almost 50% of water which was pumped from Margaret Shaft was recirculated from Dam 5. It was also supplemented by the tritium results, which indicated recent recharge that was taking place at fractures and man-made underground workings. However, hydrochemical samples at fissures from roughly 950 m below ground level indicated signatures of the mine water. Based on the analysis of the results, it was therefore, highly recommended that the water can be pumped from the shaft to reduce the shallow groundwater and seepage from the dams to prevent flooding of downstream mines. The study also highlighted the importance of environmental isotopes and hydrochemical analysis to improve the conceptual and numerical models.

Adams (2000) used isotope and hydrochemistry analysis with an aim of gaining knowledge and an understanding of the groundwater hydrochemical processes in the fractured rocks of a 3 000 km^2 catchment around the town of Sutherland in the Western Karoo. It was found that the processes such as salinisation, precipitation of mineral and dissolution, exchange of cation and human activity had a huge impact on the chemistry of groundwater in the area. The isotopes results also indicated that the occurrence of saline groundwater is as a result of the infiltration of evaporated water. The hydrochemistry analysis also noted that, in high-lying areas, the dominant water type - $Ca(HCO^3)_2$, and in low-lying areas – NaCl type; areas where water table close to the surface, soil saline are formed. During rainy seasons the salts percolates to the groundwater.

The groundwater and municipal tap water are key water resources for agriculture and domestic water use in many arid parts of the world. The study by West *et al*. (2014) attempted to establish the spatial relationship between groundwater and municipal tap water using isotopes. Groundwater, municipal tap water and rainwater samples were collected and analysed for hydrogen (^2H) and oxygen (^{18}O) in order to identify any coherent spatial pattern between groundwater and tap water isotopes that could be geostatistically-modelled across South Africa. The stable isotopes were used in groundwater and tap water samples as they are important indicators of hydrological, ecological pattern and processes. The coherent spatial structures were found in δ^2H and $\delta^{18}O$ values of groundwater and that water samples that could be predicted by geostatistical model based on simple environmental parameters. Based on the results, considerable differences were noticed in isotopic compositions of groundwater and tap water. The study concluded that the direct comparison would probably be inappropriate between recent precipitation and groundwater especially in areas where abstraction is from aquifers containing fossils groundwater. It was also recommended that to resolve these issues it is crucial to capture the spatial variability of isotopes in precipitation, the temporal variability of groundwater and tap water isotopes, as well as to improve estimates of groundwater age.

3.1.3.3 Study Area Context

The following studies were found most relevant to the current study and were categorised according to their chronological order.

Binning and Baird (2001) conducted a survey of metals in the sediments of the Swartkops River Estuary, Port Elizabeth. The concentration of Chromium (Cr), Lead (Pb), Zinc (Zn), Titanium (Ti), Manganese (Mn), Strontium (Sr), Copper (Cu), and Tin (Sn) was measured in the sediments taken from the section of the Swartkops River and estuary. The authors noted that the highest levels of concentration of metals were in both the river and estuary because of runoff from industries and informal settlements entering the system. The results from the study were compared with the results obtained 20 years ago for the estuary, which indicated the noticeable increases. According to Binning and Baird (2001), it has raised some concerns in the health aspect of the Swartkops River ecosystem, over the long term period.

In groundwater, the solubility of Uranium (U) has proved to be very sensitive in redox conditions (Vogel, 1999). The evaluation of the rate of migration of U deposition front within the Uitenhage Aquifer was conducted by Vogel *et al.* (1999). The study aimed at investigating the present position of the barrier of the Uitenhage Aquifer using isotopic signatures of U, Radium (Ra) and Radon (Rn) of the ^{238}U-series. The position of the barrier was determined using the Uranium isotopes and it was also found that the concentration of U at the barrier was reduced as it precipitates. According to Vogel *et al.* (1999) “Ra and Rn were used to evaluate the path of migration that the front of the oxygen depletion zone had taken”. At a time, the results indicated that from 28 000 years back the aquifer had no significant variations in the generalized Ra activity.

Maclear (1995) carried out a study on the groundwater Monitoring Network of Swartkops River Alluvial Aquifer in Uitenhage. The study indicated that industries of Uitenhage and Despatch had polluted the shallow alluvial aquifer. The installation of the boreholes for the monitoring network was strongly recommended as their monitoring network would assist in providing the management tool to control groundwater pollution from the Swartkops River Basin.

A groundwater quality study was also conducted in the Swartkops River Basin by Maclear (1993). The aim was to investigate the status of the existing groundwater quality in the area and the extent of pollution in the groundwater reserves. The investigation was aimed to assist the Department of Water and Sanitation and Algoa Regional Council in preparation of Water Quality Management Plan of the river basin. This investigation was triggered by the concerns of the deterioration of the water quality in the region as well as the request from industries of Uitenhage to increase the discharge effluent into the river. The results of the study revealed that the point pollution of groundwater and surface water are due to discharge from both residential areas and industries of Uitenhage and Despatch. It was, therefore, strongly recommended that in order to manage the water quality and control pollution in the area the boreholes be installed for monitoring network. The study recommended that monitoring be conducted continuously in order to have long observation records that would aid the knowledge and understanding of the existing parameters of the Swartkops River basin.

Venables (1985) conducted hydrochemistry and isotope (age dating) study covering the northern portion of Uitenhage – the Coega Artesian Basin – to evaluate the Table Mountain Sandstone (TMS) artesian aquifer in the Uitenhage area. The study also involved the following: geological and geophysical work, drilling of boreholes, aquifer testing and hydrochemical sampling. The results of the study were intended to form the basis on decision-making with regards to restriction on drilling of boreholes and reduce abstraction in the Government Water Control Area (GWCA) and redefining the boundaries of the area need to be controlled. Based on the analysis of the results obtained, it was recommended that the size of the control area be reduced and cover only the areas that are sensitive to fluctuations in piezometric level.

Parsons (1983) conducted a study using graphical methods to differentiate the water types. The boreholes delivered water of mixed origin were able to be defined as well as water derived merely from TMS and Cretaceous aquifer was also differentiated. Based on the results obtained, three major water types were recognised, i.e. water derived from TMS, Cretaceous aquifer and from mixing as a result of the leaking aquifer condition caused by the corroded casing. It was found that TMS and

Cretaceous water are mixing in the borehole. This was as a result of upward water flowing through the corroded casing and the water entered through the holes of the borehole casing.

The hydrochemical and isotope study was conducted by Talma *et al*. (1982) involved the use of carbon (^{13}C, ^{14}C) concentration and Tritium (^{3}H) for age dating of water. Another study by Talma *et al*. (1984) investigated groundwater in the Uitenhage surrounding using Isotopes. The study reported that at a time "the age of groundwater from the Uitenhage spring increase from recent to 26 000 years old near Coega and the increase confirmed that the flow direction in the central part of the Coega River was WNW-ESE", (Venables, 1985).

4. CHAPTER FOUR: METHODOLOGY

4.1 Data Collection Methods and Tools

The following methodologies were followed in order to achieve the aim as well as objectives of the study.

4.1.1 Data Collection Method

The existing hydrochemical and isotopic data as well as available information were used with the recent data to observe if there are any hydrochemical changes occurred over times. The information on groundwater level, surface water level, recharge (rainfall data) was gathered from different DWS databases and other relevant institutions.

The data for groundwater levels for monitoring boreholes were extracted from the DWS database (Hydstra and NGA) and are given in Table 2**.** The data were extracted to assess the pattern of the temporal variation of hydrogeological processes and understanding the characteristics of aquifer systems. The groundwater levels include boreholes drilled in shallow and relatively deep aquifers. The boreholes in the shallow Coega Aquifer were drilled in the Bokkeveld group, however, the boreholes: M3N0003, M3N0006 and M3N0007 penetrated the shallow aquifer group (the TMG aquifer). The boreholes in the relatively deep Swartkops Aquifer were drilled in the TMG group aquifer. The results of water level fluctuations that are presented in this report were monitored on hourly intervals; however, the data was averaged for monthly periods (Table 2). The relationship between the groundwater level elevation and surface topography of the area investigated was determined using the Bayesian Interpolation Method and correlation coefficient (R^2) was calculated.

Groundwater and surface water samples were collected at UAB in the Swartkops River catchment. Groundwater samples were collected from six borehole sites (BH1, BH2, BH3, BH4 and BH5) including the Uitenhage spring. The surface water samples were collected at upstream (S1), midstream (S2) and downstream (S3) points of the Swartkops River, as well as at discharge points of the two Waste Water Treatment Works (WWTW's). The groundwater and surface water samples were collected at the sampling points along the Swartkops River for isotope, hydrochemical, heavy metal and microbial analysis. However, the samples at WWTW's were only collected for microbial (bacteria) analysis. All these samples were collected on a quarterly basis (wet and dry season) – from November 2014 to April 2016. The heavy metal samples were only collected during the wet season.

Tritium results were used to determine the status of circulation of water within the aquifers and to determine the source, from which the water is derived. Tritium values can vary both spatially and temporally, it is therefore, imperative to establish the closest measurement of precipitation point in order to provide a reference to estimate groundwater recharge and travel times. Unfortunately, no tritium data was found at Sandveld rainfall station, hence the closest station to Sandveld (Cape Town Airport rainfall station) was used. This data was obtained from the Global Isotopic database hosted by the International Atomic Energy Agency (IAEA-GNIP, 2017). The monthly average tritium values for the rainfall station and the actual tritium values for groundwater and surface water of the study area, which were collected from the year 1961 to 2012 and 2014 to 2015 respectively, were used to estimate the recharge and age of water.

4.1.2 The Field Methods

During the sampling, the pH-EC meter was used to measure the electrical conductivity (mS/m), pH and temperature (^{o}C) of the groundwater and surface water samples. It was ensured the pH-EC meter was re-calibrated and cleaned with distilled water before it was used, for accurate reading. The Solinst dip meter was used to measure the borehole water level. The water samples were taken at five minutes intervals. When taking the sample from the borehole, the standard sampling procedure was followed, i.e. the pump was switched on for at least thirty to sixty minutes before the first sample was taken. All the samples that were collected from the springs and artesian boreholes were taken directly from the spring-eye.

The surface water samples were collected from the Swartkops River at the upstream, midstream and downstream, sampling points during the site visits.

The groundwater and surface water samples for isotopic analysis were collected using a 1-litre High Density Polyethylene bottles and were covered immediately after the sample has been taken to avoid direct sunlight and were stored in a cooler box at 40ºC before being submitted for analysis at the Environmental Isotope Group of iThemba Laboratory in Gauteng (iThemba Labs - isotope laboratory).

Hydrochemical samples were collected using a 250 ml of polyethylene sample bottles. Immediately after the samples have been taken it was ensured that the bottles are completely filled and tightened with plastic caps. The macro samples were preserved with the preservative ($MgCl_2$) and also stored in the cooler box. All information, as per site, was recorded in the booklet noting the EC (mS/m), pH and Temperature (^{o}C). Where possible, water level was also measured using the dip meter and it was measured every time the sample is taken. The sample bottles were labelled correctly per station/site.

The water samples for metal analysis were also collected in November 2015 and January 2016 of the study area. The variation in the levels of metals in groundwater and surface water samples can be a good indicator of either geogenic or human induced pollution. Samples for metal analysis were collected using 2 ml glass bottles. The samples were sent to Hydrogeology laboratory at the School of Geosciences, University of the Witwatersrand, Johannesburg.

Bacteriological samples were also collected and stored in the cooler box. The samples were also sent to the Hydrogeology laboratory at the School of Geosciences - University of the Witwatersrand.

4.2 The Analytical Methods and Procedure Followed

4.2.1 Chemical Data and Laboratory Analysis

The samples were then sent to Roodeplaat - Resource Quality Information Services (RQIS) laboratory in Pretoria for analysis. The chemical analysis was carried out as suggested by standard methods (APHA, 1995). The following major ions were analysed: Ca, Mg, Na, K, Cl, SO_4, NO_3 and F; however, Mg and Ca were analysed using titration - EDTA. The concentration of Cl in the samples was determined using Argentometric titration. The Piper diagram method (Figure 16), which is commonly used in filtering and screening large chemical data was used to interpret major anions and cations. This method explicitly defines the spatial change in water chemical composition among different environments (Domenico and Schwartz, 1998).

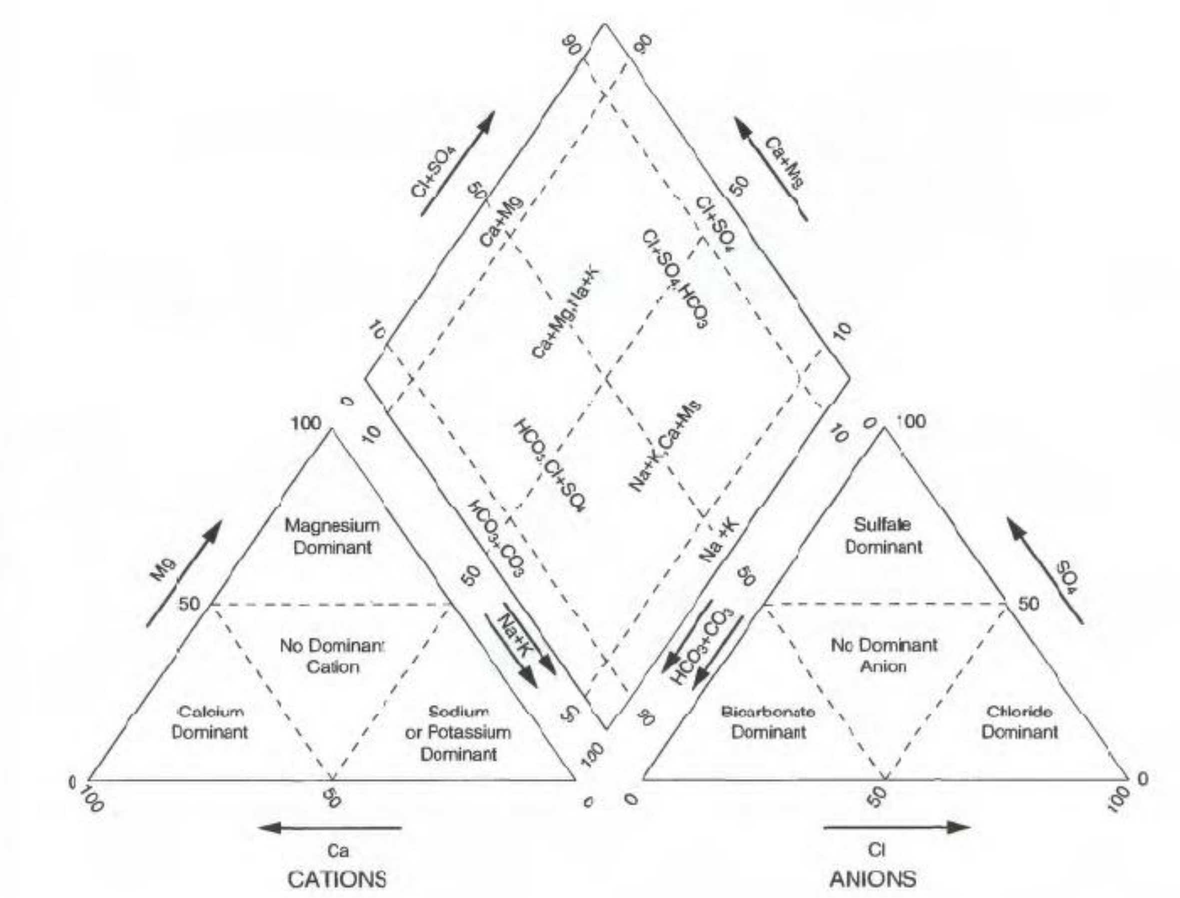

Figure 16: Water type classification (Back, 1961; Hanshaw, 1965).

The water chemistry was also represented by a Stiff Diagram (Figure 17), which is used to characterise water samples by analysing the concentration of major cations (Ca, Mg and Na+K) and anions (Cl, SO4, and HCO3). Stiff diagram was found to be useful in making comparisons of water derived from different sources and to identify the differences and similarities of water types. Cations and anions are plotted on the left and right of the vertical axis, respectively. The contamination that was derived from the same water source was studied using the same pattern. As a result, all groundwater, surface water and WWTW water samples were analysed and demonstrated in this pattern to show the evidence of contamination, Figure 17. The analysis was done to determine on how the groundwater has impacted, to what extent has the contaminants migrated to groundwater systems, what is the concentration of contaminates and what are the sources of contaminants.

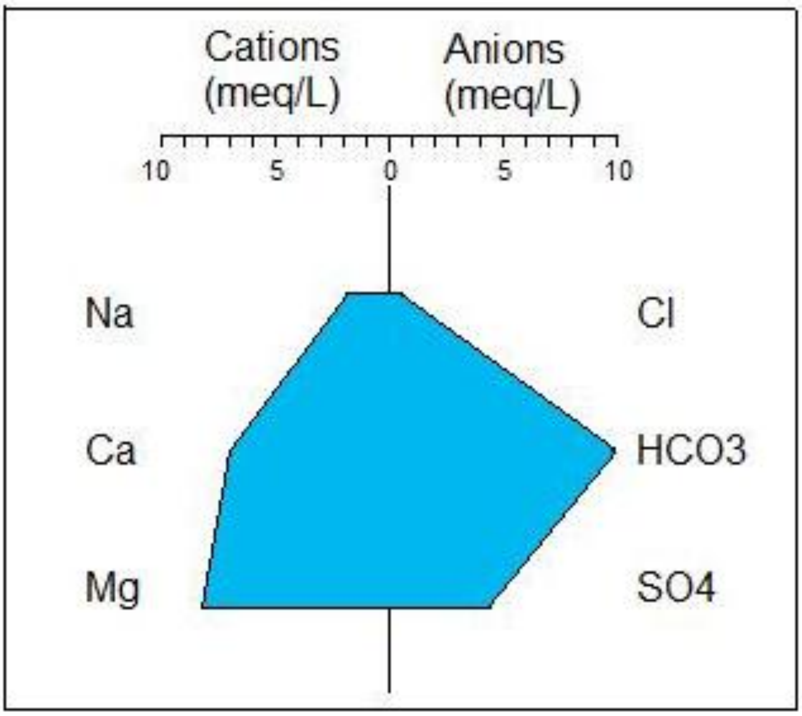

Figure 17: Stiff diagram of major ion analyses of water (Stiff, 1951).

4.2.2 Bayesian Interpolation Method

The Bayesian Interpolation method was also used to establish if is there any strong relationship between the surface topography and groundwater level elevation in the study area. This method was used in order to obtain good estimation of water levels and to establish if there are any illegal groundwater abstractions because the Uitenhage area is a Government Water Protected Area. The correlation can only exist in areas where there are static water levels. According to du Plessis (2010), the sudden variation of surface topography, groundwater abstraction and aquifer recharge may affect the results.

In order to determine the interpolation using Bayesian Interpolation method, the following information was required:

- The coordinates of several boreholes in the study area.
- Groundwater level elevation (mamsl).

In order to establish the correlation nine boreholes were selected for water level monitoring points.

4.3 Groundwater and Surface Water Interaction

4.3.1 Groundwater Flow Direction

The understanding of groundwater flow direction has critical importance for the investigation of groundwater and surface water interaction as well as pollution monitoring (Freeze and Cherry, 2002). Unlike in shallow aquifers, the flow direction of groundwater in deep aquifers generally does not reflect the surface water flow direction. In addition, the groundwater flow direction is also vital in understanding the groundwater system in terms of recharge and discharge, especially in case of gaining or losing streams (Otutu, 2010).

The groundwater flow direction was computed using surfer 8 software to gain an insight on the groundwater flow system (Figure 18). The groundwater and surface water elevations were used to construct water table maps (contour map) in order to predict the direction of groundwater flow. Eleven groundwater level monitoring borehole (Table 2) were used in the construction of the contour map, with which their longitudes, latitudes and surface elevations were measured in relation to meters above mean sea level. To determine the groundwater flow direction, the groundwater level (static groundwater level) monthly average data for November 2015 to January 2016 was used. The groundwater level (static water level) in the borehole was measured using a dip meter. The actual static water levels in relation to mean sea level of different locations were obtained by subtracting the borehole groundwater level depth from surface elevations, in relation to mean sea level. The static water level values were contoured using longitudes and latitudes in surfer 8 software. The lines on Figure 18 represent the water table contours and groundwater flows from the highest contour line values to the lowest contour line values. The flow direction is perpendicular to the contour lines. The colours on the map represent the magnitude/ intensity of groundwater flow (Otutu and Oviri, 2010).

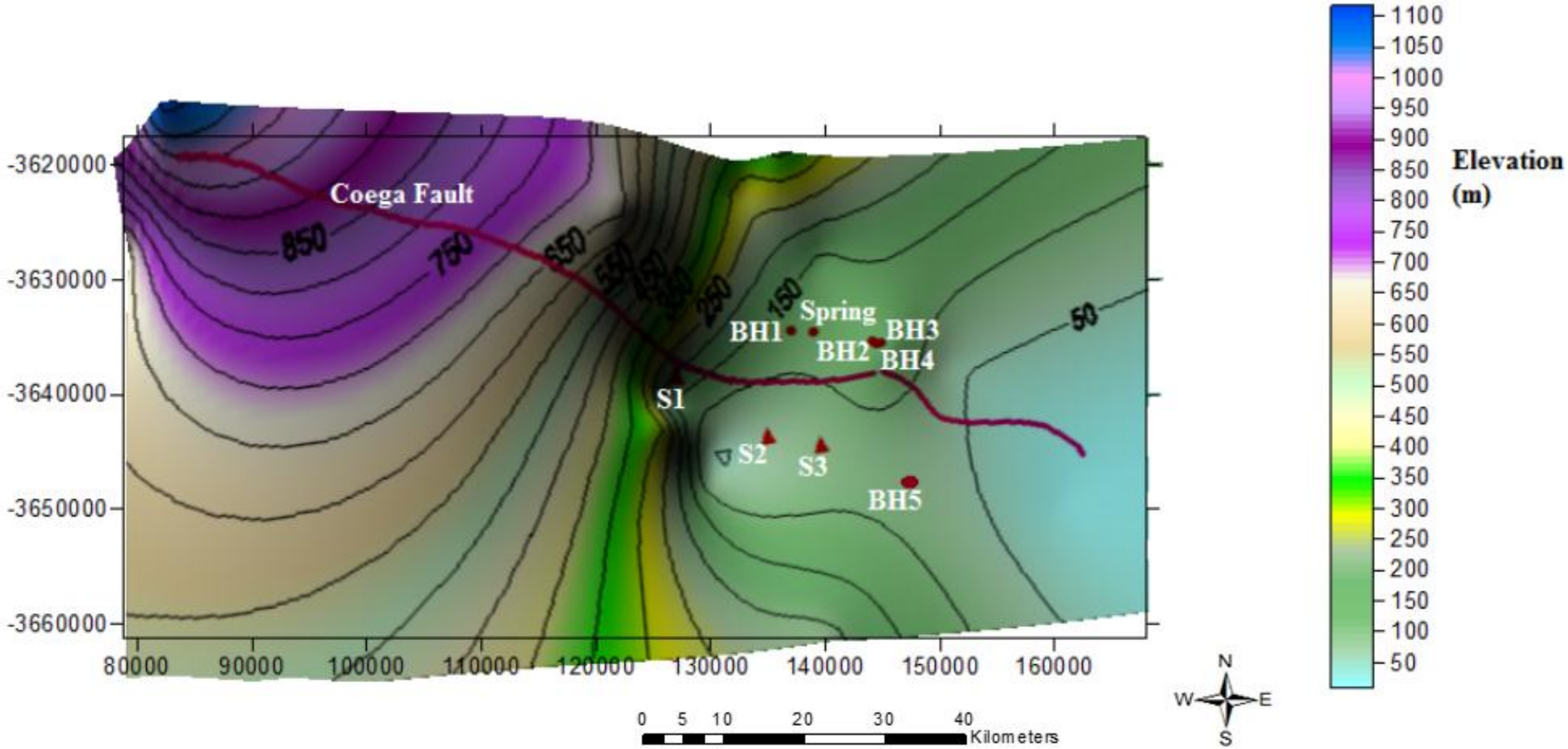

Figure 18: Uitenhage groundwater contour map of the study area, using surfer 8 software.

4.3.2 Stable Isotope Analysis and Laboratory Methods

The isotopic composition of ^{18}O and ^{2}H data was used to evaluate the connectivity of water from the different water systems and it is given in per mil (‰) deviation from Standard Mean Ocean Water (SMOW: Freeze *et al*. 2002; Clark *et al*. 1997). The global Meteoric Water Line (GMWL), equation: $\delta^2H=8\delta^{18}O+10$(‰) (Craig, 1961) and Local Meteoric Water Line (LMWL), equation: $\delta^2H=5.8\delta^{18}O+5.2$ (‰) (Van Wyk, 2010) were used in the interpretation of isotopic data as a result of linear regression of $\delta^{18}O$ and δ^2H data water samples.

The stable isotope water ratios of D/H ($^2H/^1H$) and $^{18}O/^{16}O$ were analysed at the iThemba Labs, Gauteng and School of Geosciences, University of the Witwatersrand. Analytical results were presented in delta-notation. The equipment used for stable isotope analysis consists of a Thermo Delta V mass spectrometer connected to a Gas bench. Equilibration time for the water sample with hydrogen as well as with CO_2 is 40 minutes and twenty hours respectively. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. In term of the analytical precision, the O and H content were estimated to be 0.2‰ and 0.8‰, respectively.

4.3.3 Water Microbiology Data and Laboratory Analysis

Water samples for bacteriological analysis that were collected in November 2014, June 2015, August 2015 and January 2016 were analysed for Enterobacter Aerogenes, Proteus Mirabilis and Escherichia Coli (E. Coli) using the Most Probable Number (MPN) technique (SABS) and the results were expressed as MPN/100 ml.

5. CHAPTER FIVE: THE ESTABLISHMENT OF A RELATIONSHIP BETWEEN SURFACE TOPOGRAPHY AND GROUNDWATER LEVEL ELEVATION BY USING BAYESIAN INTERPOLATION METHOD

5.1 Results

Surface Topography and Groundwater Level Elevation

The relationship between the groundwater level elevation and surface topography of the area investigated was determined using the Bayesian Interpolation Method and correlation coefficient (R^2) was calculated using equation in Figure 19 and the correlation coefficient of 0.9953 was established. The results indicated the strong relationship between surface topography and groundwater level elevations in the study area, in both aquifers.

Table 2: Groundwater level monitoring data of the existing monitoring network; the borehole geographic coordinates, borehole depth, measured depth as well as the surface elevation and groundwater level elevation.

Site No.	Borehole Aquifer type	Longitude (East)	Latitude (South)	Borehole depth (mbgl)	Static water level (m)	Surface Elevation (mamsl)	Groundwater Level Elevation (mamsl)
M1N0003	TMG	25.33086111	-33.78961111	n/a	21.690	95.000	73.310
M1N0004	TMG	25.32944444	-33.80113889	182.900	8.767	81.000	72.233
M1N0034	TMG	25.30125	-33.74361111	258.000	32.859	195.000	162.141
M1N0036	TMG	25.331361	-33.777611	152.000	16.916	73.000	56.084
M1N0038	TMG	25.34147222	-33.80227778	157.000	39.510	112.000	72.490
M3N0001	Bokkeveld	25.27302778	-33.64422222	91.200	20.036	684.000	663.964
M3N0002	Bokkeveld	25.45363889	-33.64716667	115.520	3.537	143.000	139.463
M3N0003	TMG	25.45094444	-33.64305556	188.480	13.032	169.000	155.968
M3N0004	Bokkeveld	25.38683333	-33.59675	31.920	7.714	285.000	277.286
M3N0006	TMG	25.55813889	-33.73555556	53.100	3.467	62.000	58.533
M3N0007	TMG	25.5800000	-33.73786111	128.000	0.000	52.000	52.000

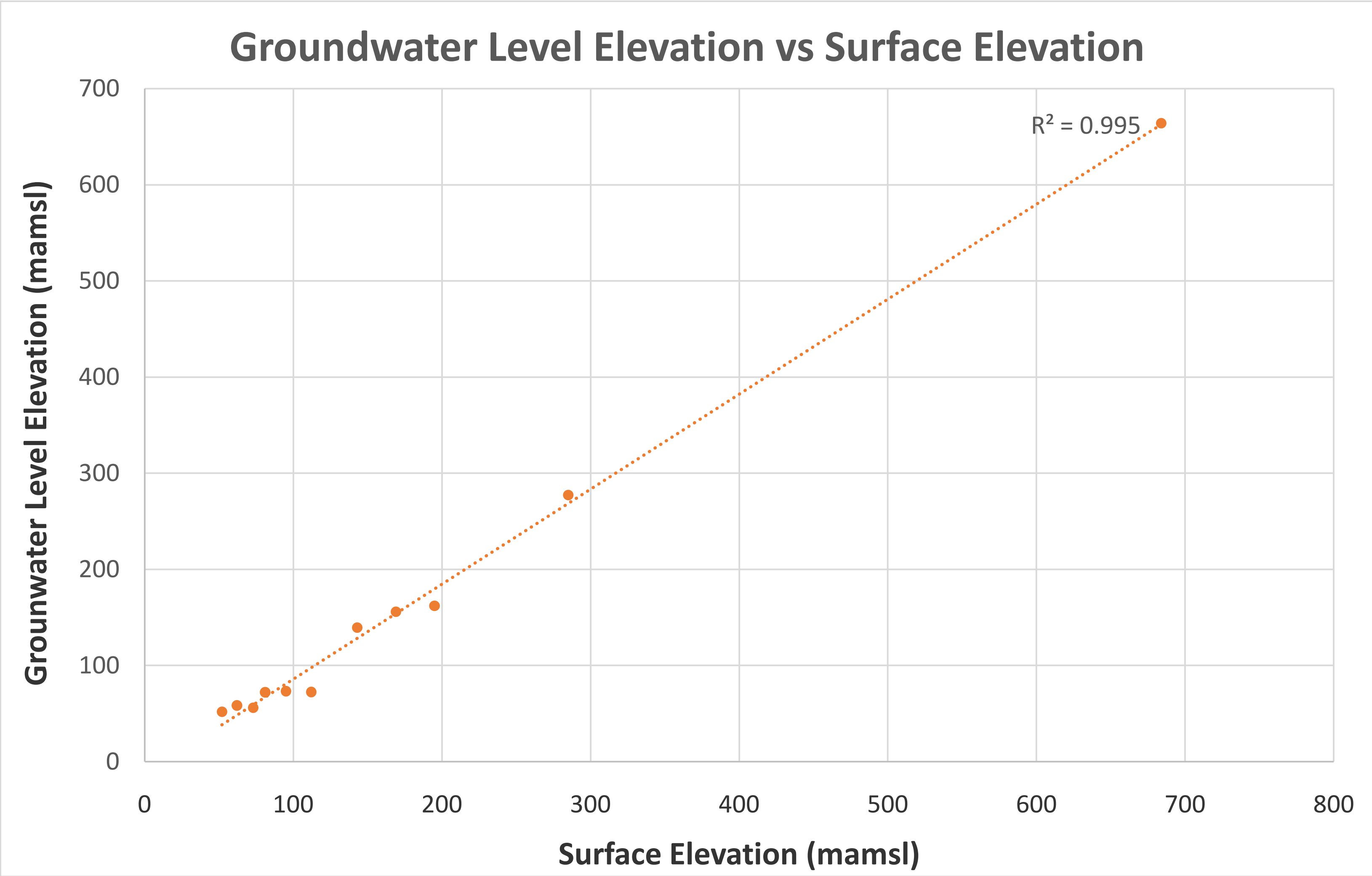

Figure 19: Groundwater Level Elevation vs. Surface Elevation.

The following boreholes: M3N0001, M3N0002, M3N0003, M3N0004, M3N0006, and M3N0007 were drilled in the Coega Ridge Aquifer, whilst M1N0003, M1N0004, M1N0034, M1N0036 and M1N0038 were drilled in the Swartkops Aquifer. Figure 20 shows that there is a strong relationship between groundwater level elevations and surface topography, which indicates that both aquifers are shallow, however, Swartkops Aquifer is relatively deep as compared to Coega Ridge Aquifer. The groundwater levels increases as the surface elevation increases, which is an indication that groundwater levels are closer to the surface. This exhibits that groundwater elevation mimics the topography and groundwater flows towards the directions of the surface water depending on the slope.

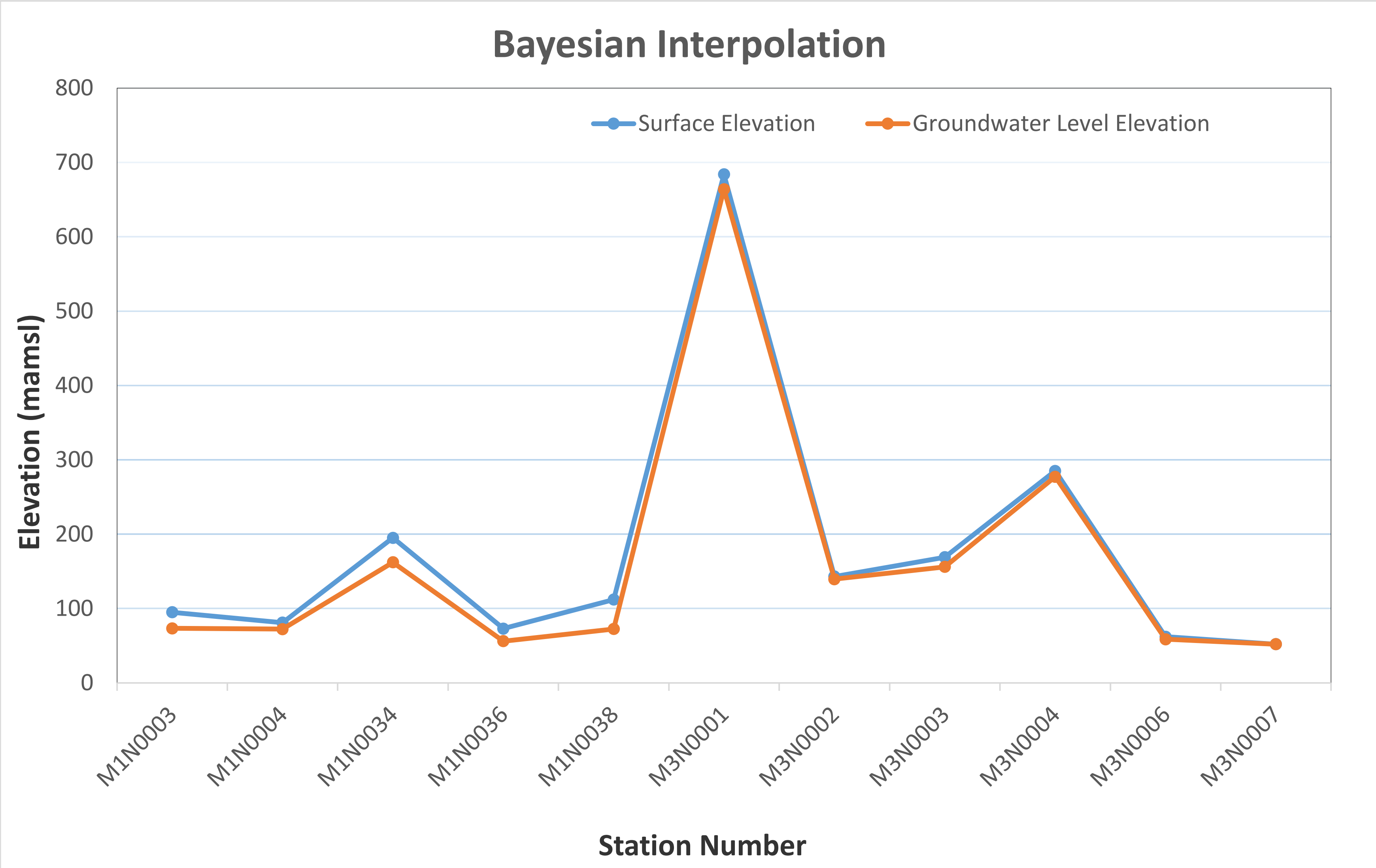

Figure 20: Shows Bayesian Interpolation Conceptual Model.

5.2 The determination of groundwater flow direction using surfer 8 software.

The groundwater elevation contour map (Figure 21) of the study area shows that the direction of the groundwater in the alluvial aquifers is towards the easterly direction, following the topographic gradient, towards the Blue Water Bay, Indian Ocean. The aquifer systems of the Uitenhage area consist of four major hydrological units (Figure 29). The two aquifers, Swartkops and Coega Aquifers are divided by the Coega Fault. The fault acts as a path way for groundwater flow and due to the difference in hydraulic gradient, pollutants could not migrate from Swartkops Aquifer to the Coega Aquifer. However, groundwater does flow from the Coega Ridge Aquifer through the fault to the Swartkops Aquifer. This is probably due the artesian condition of Coega Aquifer and surface elevation, which decreases from west to east. The contours show that fault is permeable and has no impact on groundwater circulation. Figure 21 shows the vectors in the map that represent the groundwater flow direction.

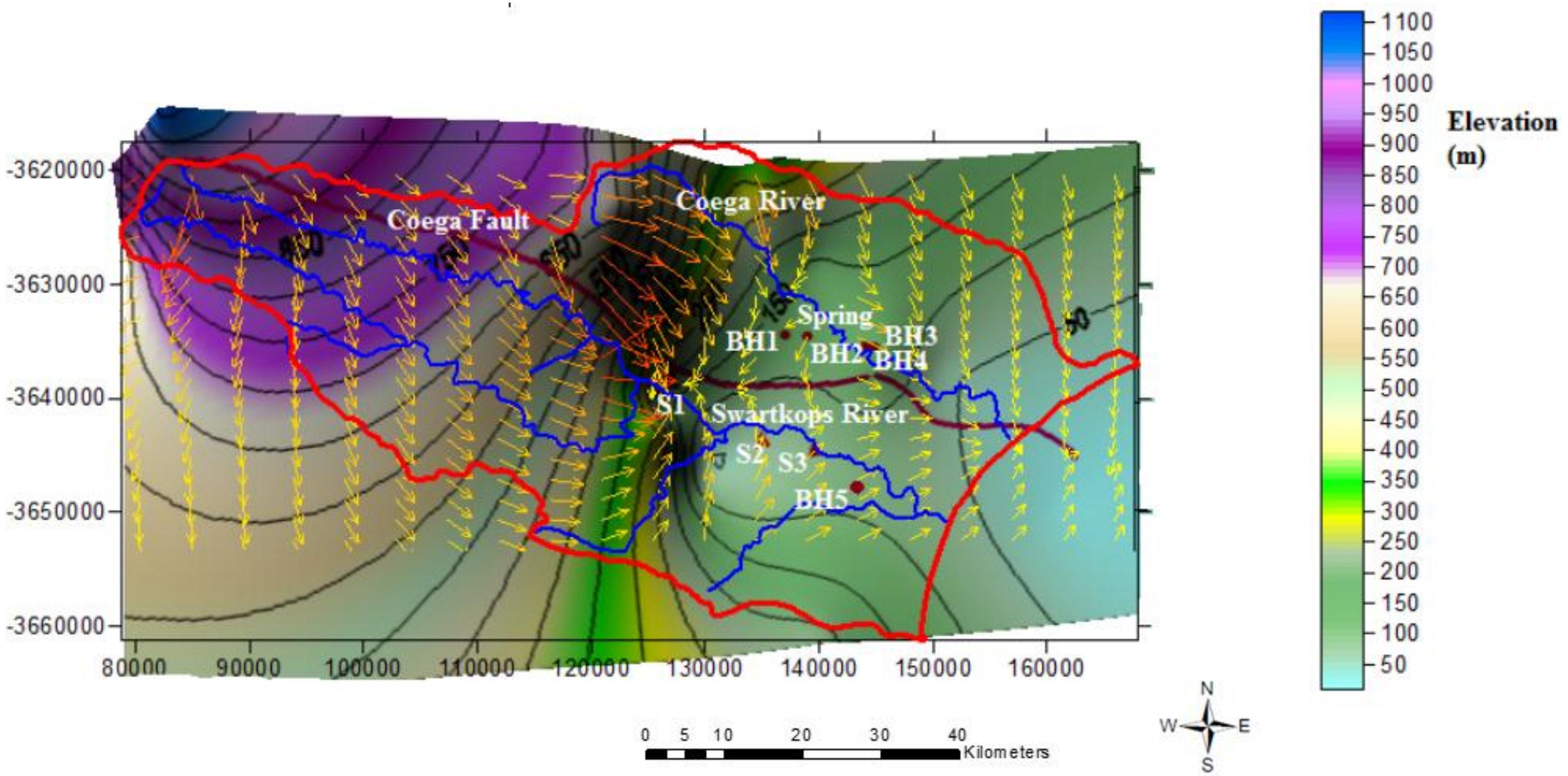

Figure 21: Contour map showing groundwater flow direction in the study area

6. CHAPTER SIX: TO ESTABLISH GROUNDWATER-SURFACE WATER INTERACTION USING ENVIRONMENTAL ISOTOPE ANALYSIS, BACTERIOLOGY AND TRACE METALS

6.1 The determination of groundwater and surface water recharge using the isotope tracers (^{18}O, ^{2}H and ^{3}H)

Isotopes of 18-Oxygen (^{18}O) and Hydrogen (^{2}H)

The results of isotopic analyses for five periods/sampling campaign (i.e. November 2014, February 2015, June 2015, August 2015 and November 2015) are shown in Table 3 and Figure 22. The Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL) based on the Sandveld station, which indicate precipitation with slopes s=8 and s=5.8, respectively, are also shown in Figure 22. The plot (Figure 22) indicated that the isotopic analyses data points are clustered into five separate groups, i.e. Group A to Group E.

Table 3: Analytical Results of Environmental Radiogenic Tritium and Stable Isotope Data (SMOW).

Site ID	Altitude (m)	Date	δ D (‰)	δ ^{18}O (‰)	Tritium (T.U)		Cl (mg/L)
BH3	139	Nov. 2014	-20.28	-5.06	0.3	±0.2	37.4
BH4	127	Nov. 2014	-23.54	-5.25	0	±0.2	4894.5
BH2	116	Nov. 2014	-21.3	-5.14	1.4	±0.3	35.9
BH1	225	Nov. 2014	-19.1	-4.69	0	±0.2	86.3
Spring	176	Nov. 2014	-17.43	-4.82	0	±0.2	32.9
S1	138	Nov. 2014	-12.13	-3.17	1.4	±0.3	44.2
S2	41	Nov. 2014	-8.14	-2.12	1.2	±0.3	251.6
BH3	139	Feb. 2015	-20.84	-5.44	0.3	±0.2	39.3
BH4	127	Feb. 2015	-22.76	-5.67	0	±0.2	37.2
BH2	116	Feb. 2015	-20.03	-5.16	0.2	±0.2	-
BH1	225	Feb. 2015	-19.19	-4.69	1.1	±0.3	79.1
Spring	176	Feb. 2015	-18.9	-5.25	0	±0.2	34
S1	138	Feb. 2015	-6.38	-2.28	2.1	±0.3	45.1
S2	41	Feb. 2015	-4.18	-1.49	2.3	±0.3	453.5
S3	28	Feb. 2015	-4.45	-1.13	1.5	±0.3	336
BH3	139	Jun. 2015	-25.9	-4.73	0	±0.2	37.9
BH4	127	Jun. 2015	-27.5	-4.96	0.6	±0.2	-
BH1	225	Jun. 2015	-25.7	-4.49	0.5	±0.2	83.3
Spring	176	Jun. 2015	-23.8	-4.62	0.8	±0.2	34.6
S1	138	Jun. 2015	-17.7	-3.43	2.0	±0.3	41.4
S2	41	Jun. 2015	-11.5	-2.61	1.3	±0.3	469.2
S3	28	Jun. 2015	-15.9	-2.49	1.8	±0.3	488.3
BH3	139	Aug. 2015	-19.4	-3.34	0.2	±0.2	35.6
BH1	225	Aug. 2015	-18.5	-3.13	0.9	±0.3	288.3
BH5	20	Aug. 2015	-12.8	-1.67	1.8	±0.3	1229.1
Spring	176	Aug. 2015	-16.6	-2.81	0	±0.2	32
S1	138	Aug. 2015	-14.2	-2.66	1.4	±0.3	33.4
S2	41	Aug. 2015	-14.3	-2.26	1.9	±0.3	127.1
S3	28	Aug. 2015	-9.3	-1.3	2.6	±0.3	483
BH3	139	Nov. 2015	-19.2	-3.28	0.1	±0.2	55.3
BH4	127	Nov. 2015	-21.3	-3.5	0.8	±0.2	2275.5
BH1	225	Nov. 2015	-17.6	-2.5	0.5	±0.2	155
BH5	20	Nov. 2015	-11.1	-0.96	2.3	±0.3	1217.6
Spring	176	Nov. 2015	-16.3	-3.03	2.3	±0.3	41.1
S1	138	Nov. 2015	-12	-2.04	2.1	±0.3	47.6
S2	41	Nov. 2015	-14.3	-2.75	2.1	±0.3	141.7
S3	28	Nov. 2015	-5.3	-0.47	3.3	±0.4	445.8

The groundwater samples as well as the spring water sample collected in November 2014 and February 2015 (Group B) are relatively isotopically less enriched with heavy isotopes signatures as compared to the water samples collected in June 2015(Group C), i.e. they plot above LMWL. They probably represent the rainfall water or local shallow groundwater circulation with no evaporation. The surface water samples for S1 (upstream) in November 2014 and February 2015(Group A), plots on GMWL indicating the impact of rainfall water; however, S2 (midstream) in November 2014 and February 2015 (Group A) plot very close to LMWL indicating the impact of the rainfall as well as slightly evaporation. S3 (downstream) in February 2015 indicated high evaporation (Group E).

All groundwater samples and the spring water sample collected in June 2015 (Group C) plot below LMWL, which indicates that the recharge took place when the evaporation process was also occurring. As a result, the water samples are more enriched with less heavy isotopes signatures. The other factor that may have caused the depletion is isotopic fractionation, which is greater at low temperature, i.e. $\delta^{18}O$ values are more negative in winter. The clustering of groundwater samples indicates the deep groundwater circulation as well as seasonal change. This was expected during the winter season as the water table is usual lower.

The surface water samples collected in June 2015 were clustered with the samples in Group D, which were more enriched with heavy isotopes signatures as compared to groundwater samples for the same month. The surface water samples clustered together with the groundwater samples collected in August 2015 and November 2015 (Group D), however, S2 water samples collected in August 2015 and November 2015 (Group D), also depleted with relatively the same magnitude as groundwater samples for the same months. This was probably caused by the seasonal change from winter to summer. The isotopic composition of the S2 water samples collected in August 2015 and November 2015 (Group D) in relation to other river water samples for the same period was probably due to damming effect of the river at that point which increases concentration of isotopes molecules resulting from higher water volume and the bathymetric characteristics of the dam due to variation in sediment fluxes. This could be also probably due to groundwater mixing with surface water, i.e. the groundwater discharging to surface water during that season, which was mixed with water that was slightly exposed to low evaporation.

The samples collected in June 2015, which are in Group C, were more depleted as compared to August 2015 and November 2015 (Group D). This concurs to the expectation that the isotopes molecules least depleted before groundwater recharges during this season .i.e the evaporation was expected to be very low. In addition, owing to temperature effect, isotope ratios of winter rainfall are lower than of the summer rainfall (Clark and Fritz, 1997, Datta et al. 1991).

The surface water samples S1 and S3 as well as samples collected from the borehole - BH5 at Despatch in August 2015 and November 2015 (Group E) shows a greater evaporation than other groundwater samples and spring water sample for the same period. The results indicated that the isotopic composition of groundwater from borehole BH5 was related to the river water; there was a significant deflection from LMWL in relation to all other points. The samples were characterised by heavy isotopes signatures and this was probably due to high evaporation occurring during these months (summer season) and other climatic conditions such as high temperatures that was associated with drought, which was experienced at a time. The BH5 is nearby the Swartkops River, therefore, was possibly recharged by the surface water (river water) via bank infiltration, which was exposed to high evaporation before the recharge.

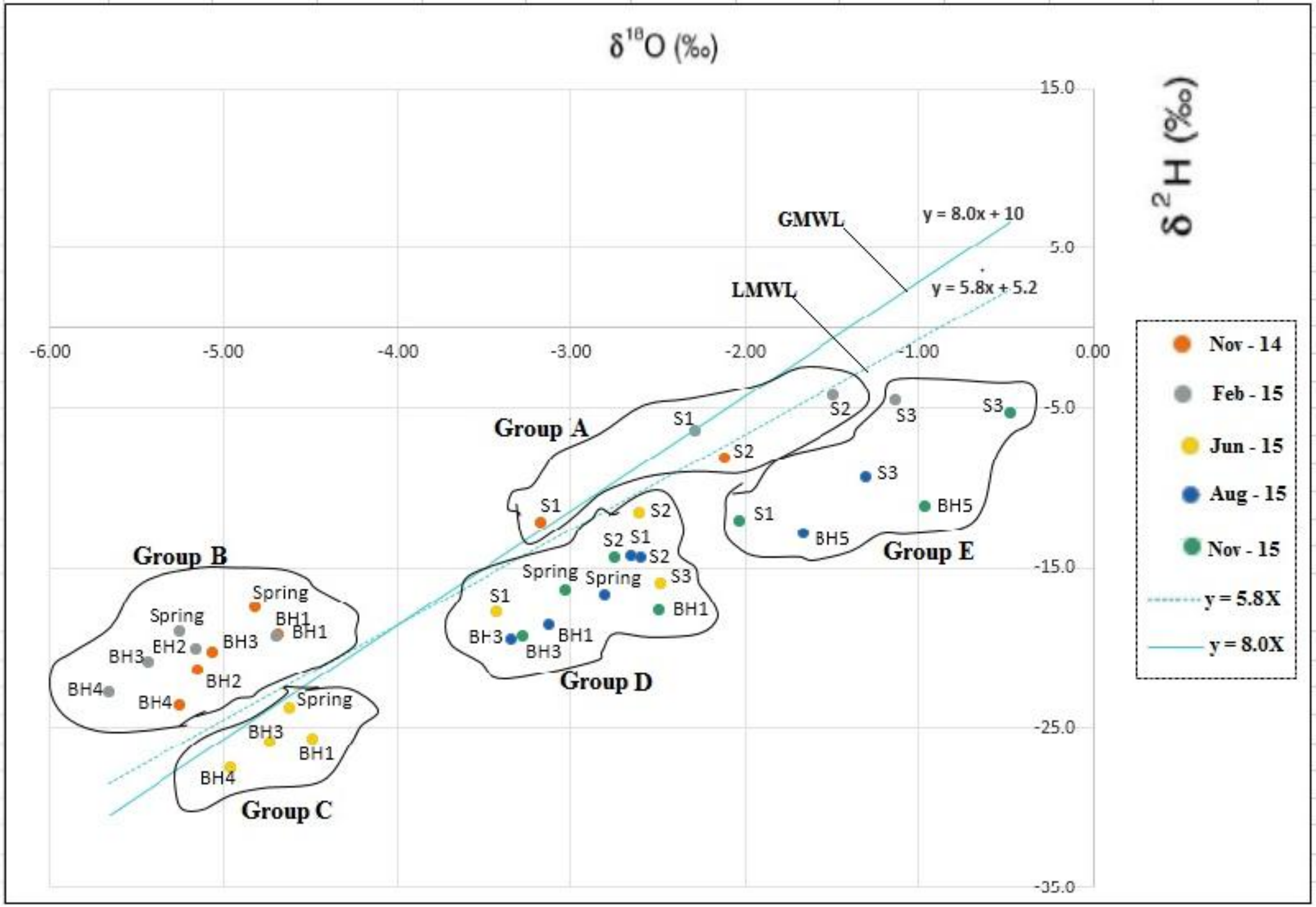

Figure 22 : $\delta^{18}O$ vs. δD plot in relation to the Global Meteoric Water Line (Craig, 1961) and Local Meteoric Water Line (LMWL in Sandveld).

Figure 23 shows high concentration of chlorine in BH4 with less enriched in heavy isotopes (^{18}O) and BH5 enriched with heavy isotopes. The high concentration of chloride in the borehole- BH4 was noted only in November 2014 and November 2015, which was probable due to irrigation return or discharge of deep groundwater.

The high concentration in BH5 was also probable due to the influence of the stream, which was influenced by industries (Uitenhage and Dispatch) and sewage treatment works that are discharging directly to the stream (river); owing to the fact that high concentration was noted at the S2 and S3 of the Swartkops River where Kwalanga WWTW is discharging, it was supported by the result of previous studies, such as Maclear (1993), Maclear (1995) and Binning and Baird (2001). The pollutants were probably due WWTW. The sample collected from the WWTW at Kwalanga (Table 6) concentration was noted to be high (1499.90 mg/L). As a result, the BH5 was drilled ± 700m away from the stream, the borehole is expected recharged by the stream through bank infiltration, which was also supported by the isotope results.

The shallow groundwater aquifer (Swartkops) was more enriched in heavy isotopes (^{18}O) and consists of high concentration of chlorine, which indicated the interaction of deep groundwater circulation and surface water. However, artesian aquifer (Coega) indicated high concentration of chlorine and depleted ^{18}O values, which indicated deep groundwater circulation with long residence time. As it was indicated above that there was no influence of the fault, groundwater does flow from Coega Aquifer through the fault to Swartkops Aquifer; however, groundwater does not flow from Swartkops Aquifer to Coega Aquifer as a result of unfavourable gradient conditions.

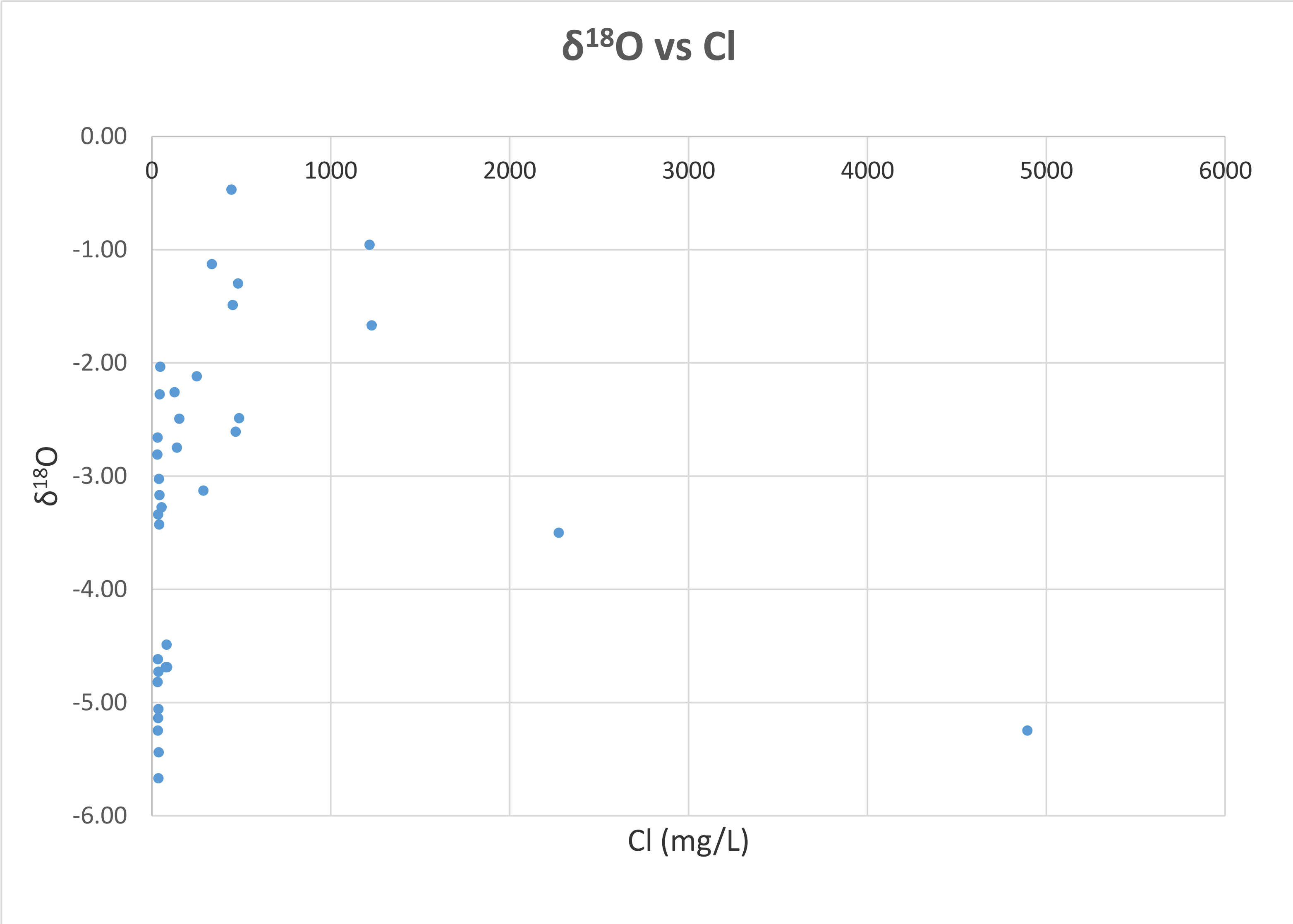

Figure 23: Relationships between chloride (Cl) and $\delta^{18}O$ for stream water, groundwater and spring water.

Tritium (^3H)

The average monthly tritium data of the Cape Town rainfall station for the year 1961 to 2012 were plotted in Figure 24. The plot indicated the decline in the tritium trend, from about 56 TU in 1961 to 2.0 TU in 2012. Tritium values from the Cape Town rainfall station were compared with those used in the current study as means of evaluating water composition as well as the age of water.

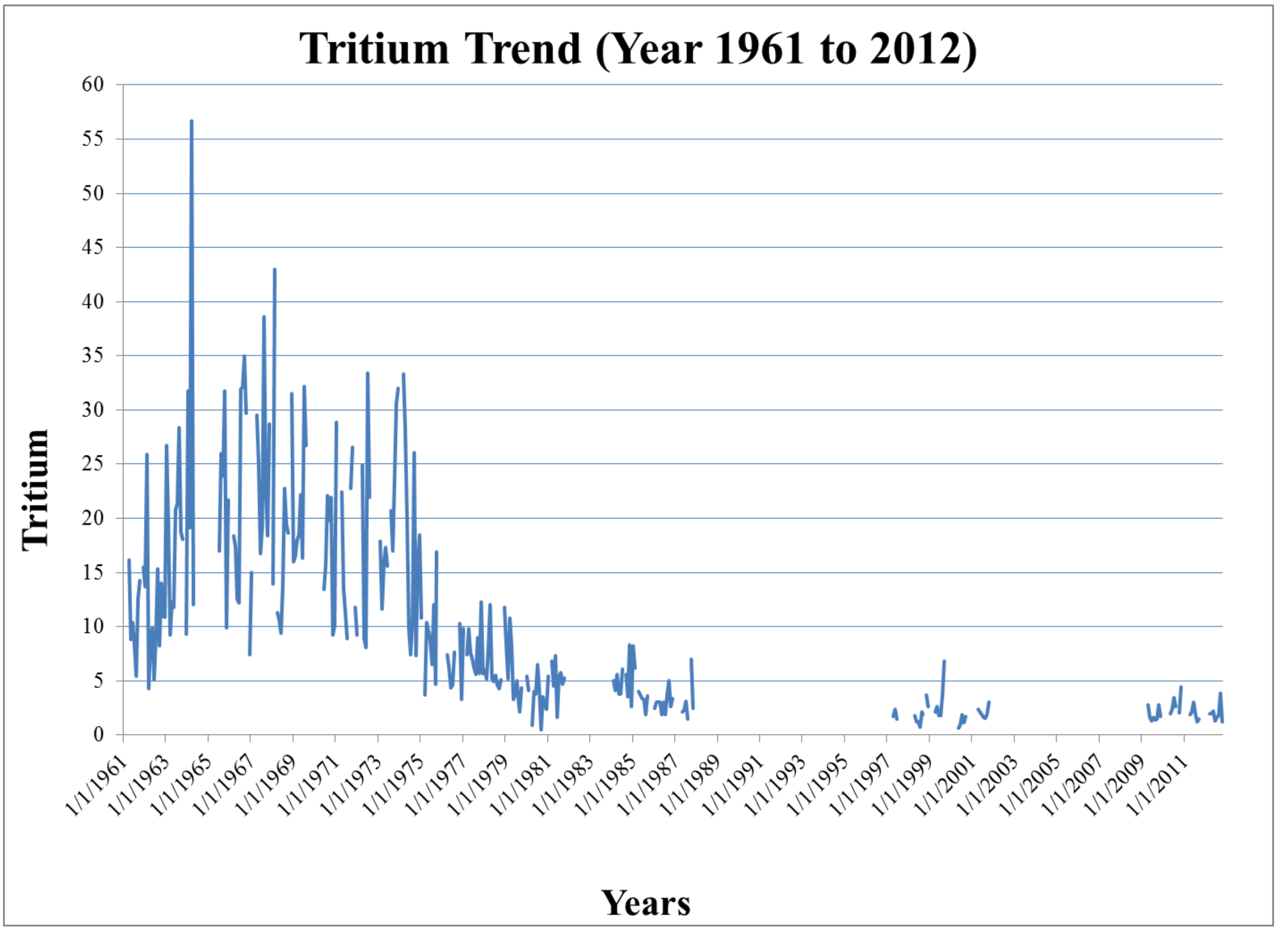

Figure 24: Tritium trend at Cape Town rainfall station from year 1961 to 2012 (IAEA-GNIP, 2017)

The results of the tritium concentrations were shown in Table 3 and Figure 25. Figure 25 shows the mixing pattern of tritium concentration for both groundwater and surface water samples. Generally, low tritium values indicate water with long circulation time or deep groundwater circulation whereas higher values signify young or sub-modern water, predominantly in the shallow aquifer or recharge directly from rainfall.

The surface water samples in November 2014 yielded the concentration of 1.4 TU for S1 and 1.2 TU for S2. The surface water samples indicated the recent recharge, which was mixing with groundwater emanated from the mountains (high altitude areas). This was probably due to seasonally variation.

The groundwater samples yielded the concentration of 0TU for BH1, 1.4TU for BH2, 0.3TU for BH3, 0TU for BH4 and 0TU for the Uitenhage spring. All groundwater samples indicated the deep groundwater circulation pattern apart for BH2, which is an artesian borehole; this could be an indication of the mixing of recently recharged water with deep groundwater.

In February 2015, the concentration of tritium in surface water samples were 2.1 TU for S1, 2.3 TU for S2 and 1.5 TU for S3. The high concentration of tritium indicated a direct recharge from rainfall. The samples of groundwater yielded the tritium concentration of 0 TU for spring, 1.1 TU for BH1, 0.2 TU for BH2, 0.3 TU for BH3 and 0 TU for BH4. It is evident from the figure that the majority of groundwater samples have lower tritium concentration compared to surface water samples. The tritium concentration in groundwater indicted that the boreholes tap water from deep groundwater, however, the BH1 could be recharged from recent water derived from highlands, as it was drilled in the TMG outcrop.

The concentration of tritium in June 2015 water samples for S1 was 2.0 TU, S2 was 1.3 TU and S3 was 1.8T U. The high concentrations of tritium were noticeable, which in this case were also possibly indicating recent recharge from the surrounding high areas. The concentration of tritium in the Uitenhage spring was 0.8 TU, BH1 was 0.5 TU, BH3 was 0 TU and BH4 was 0.6 TU. The relatively high concentration of tritium in groundwater samples, including the spring, indicated deep groundwater circulation mixing with shallow groundwater. This indicated that the aquifer could be recharged from the high areas or it could be, as results of seasonal change. However, the zero tritium concentration in BH3 indicated water originating from deep groundwater water circulation.

In August 2015, the tritium concentrations in surface water samples were 1.4 TU for S1, 1.9 TU for S2 and 2.6 TU for S3. As the case in June 2015, the high tritium concentration was probably an indication of the recent recharge from the winter rainfall. The surface water might also be mixing with groundwater derived from the mountains. The groundwater samples had relatively low concentration of tritium, which were 0.9 TU for BH1, 0.2 TU for BH3, 1.8 TU for BH5 and 0TU for Uitenhage Spring. The deep water circulation was again the cause of low tritium as it was seen in other seasons as well for in BH3 and spring. In the case of BH1, it was probably due to the same reason as that of February 2015, i.e., recent recharge that was emanating from the highlands. In the case of BH5, it was drilled next to the Swartkops River, therefore, was possibly recharged by the surface water (river water) via bank infiltration. This was an indication of the interconnection between the surface water and groundwater.

The high concentration of tritium was noticeable in surface water samples for November 2015 and the concentrations were as follows: 2.1 TU for S1, 2.1T U for S2 and 3.3 TU for S3. This was probably due to recent rainfall (winter rain). The tritium concentration was also high in BH5 (2.3TU) and Uitenhage spring (2.3TU). In the case of BH5, it was probably due to the same reason as in August 2015, i.e., recharged via bank infiltration. The other groundwater samples yielded the tritium concentration as follows: 0.5 TU for BH1, 0.1 TU for BH3 and 0.8 TU for BH4. The relatively high tritium concentration of BH1 indicated the recent recharge from the mountains as in the case of all other months where samples were collected, except for November 2014. For BH5, it was again due to recharge from the river as in the case of August 2015.

The results of the tritium indicated the limited interaction between the Swartkops River and BH5. It was revealed that the Swartkops River was recharged from groundwater emanating from the mountains, which in turn recharged BH5. There was no interaction established between the other boreholes and Swartkops River. This was expected since there are located on the other side of the fault (Coega Artesian Aquifer) due to the groundwater flow gradient as it was indicated in section 5.2. This indicates that again the fault only acted as a pathway for groundwater flow from Coega to Swartkops Aquifer; as a result, the Coega Aquifer was not vulnerable to the pollution of Swartkops Aquifer.

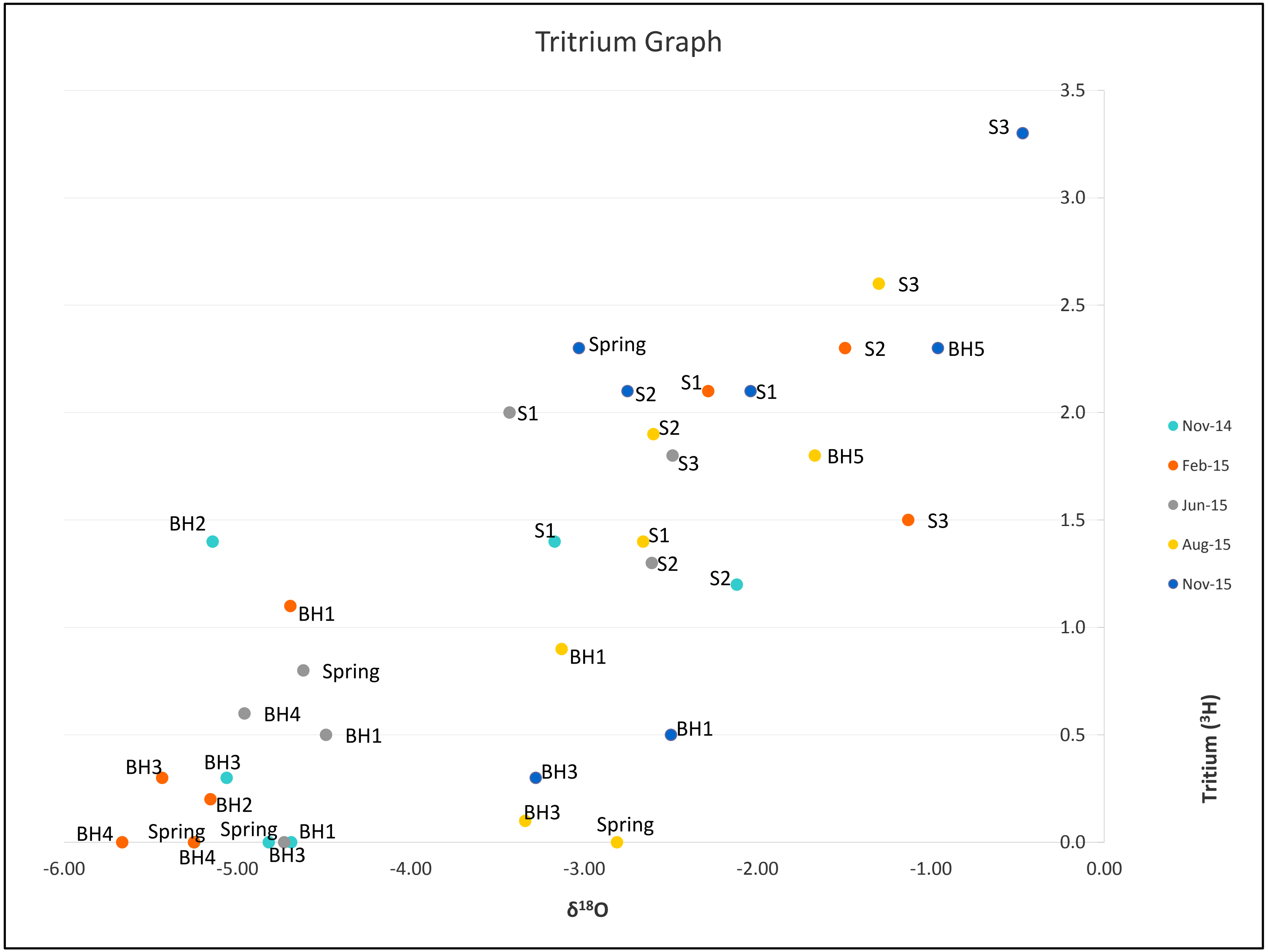

Figure 25: Mixing pattern of deep circulation and low ^{3}H water vs shallow circulating high tritium water.

6.1 Hydrochemical analysis

The sample gives an overview of the water quality during the period of November 2014 to January 2016 (Table 6, Appendix A). Groundwater, surface water and WWTW samples were analysed in the RQS Laboratory (DWS-Pretoria). The nature and change in water type (characteristics) was illustrated using the piper diagram. Figure 26 represent the groundwater and surface water chemistry data of the study area. Based on the plot, chemical analyses of groups of water samples from various localities in the TMG aquifer, the diamond field of the Piper diagram shows Na-Cl type of water except BH4, which indicated the high salinity in the chemical properties of water. The water type is that dominated by Na-Cl water, which is typical old marine water deep groundwater type. The chemistry signature indicates that water has undergone significant ion exchange because of the long residence time in the aquifer. The sample from the BH4 only in June 2015 plotted on the Ca-Cl-SO_4 dominated water type zone. BH4 water sample indicated that the water was typical of mine water environment, which it was not clear since there were no mining activities. The surface and groundwater samples plotted within the same position within diamond shape and both showed the attributes of being deep groundwater type. This means that there is an interaction between groundwater and surface water resources.

6.2 Physical chemistry

The electrical conductivity for BH4 was also very high ranging from 734 to 1402 mS/m. All the parameters in BH4 were noted to be high (Table 6), which exceed the maximum acceptable limit of 70 mS/m of water quality guidelines - Second Edition (1993) for domestic use. These guidelines were set by the Department of Water Affairs and Forestry in 1993. The high concentration was probably due to influence of underlying geology. The BH5 electrical conductivity exceeded the maximum allowable standard of 300 mS/m to 444 mS/m in November 2015 and other parameter also noted to be high. This was probably due to some other activities that might be occurring in vicinity of the borehole within the settlement and industries. The isotopes results indicated that the borehole (BH5) was receiving water from the Swartkops River, which is also polluted. This was also supported by the studies done by Maclear (1993), Maclear (1995) and Binning and Baird (2001). The electrical conductivity of surface water samples for WWTW at Kwalanga and S2 in November 2015 were 572 mS/m and 508 mS/m, respectively. This was probably due to the WWTW at Kwalanga that is discharging directly to S2 monitoring point.

The spring water samples indicated low TDS ranging from 91.12 mg/L to 97.30 mg/L showing low ion concentration, which indicates relatively fast groundwater circulation in mountains (Adelana, *et al*., 2010). The borehole BH1 also indicated fast groundwater circulation with low ion concentration and also relatively variable isotopic composition, however, the significant change in TDS (ranging: 728.96 mg/L to 1583.21 mg/L) values were only noted in August 2015 and November 2015, which indicated that the deep groundwater circulation was mixing with fast groundwater circulation in the mountains.

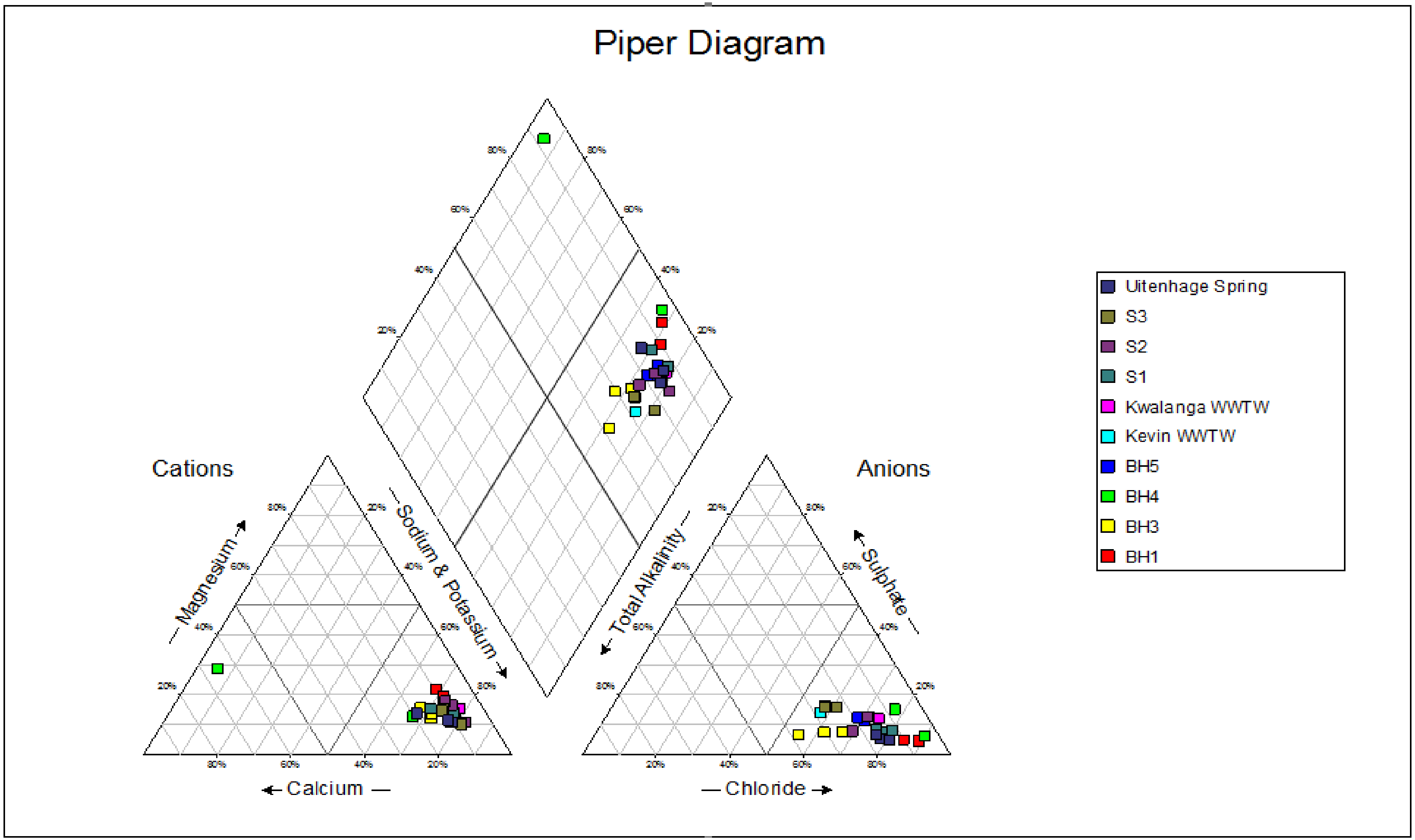

Figure 26: Piper Diagram of the Uitenhage Water Samples

The water chemistry was also represented in a Stiff Diagram (Figure 27) in order to characterise water samples by analysing the concentration of major cations (Ca, Mg and Na+K) and anions (Cl, SO_4, and HCO_3). The plot on Figure 27 represents average values of ten water samples for both groundwater and surface water samples including WWTW water samples. The BH5, S3 water sample as well as Kevin and Kwalanga WWTW water samples have funnel shapes, which indicated the relatively high Na-Cl and Mg-HCO_3-SO_4 with relatively low Ca concentration. The BH4 also had funnel shape but indicated Na-Cl and Ca-Mg-SO_4 with low concentration of HCO_3. The BH1 and S2 water samples indicated the Na-Cl with relatively low Ca-HCO_3 concentration but no concentration of Mg-SO_4. BH3 water sample only indicated very low concentration Na-Cl water type. Uitenhage spring and S1 water samples indicated only very low concentration of Cl.

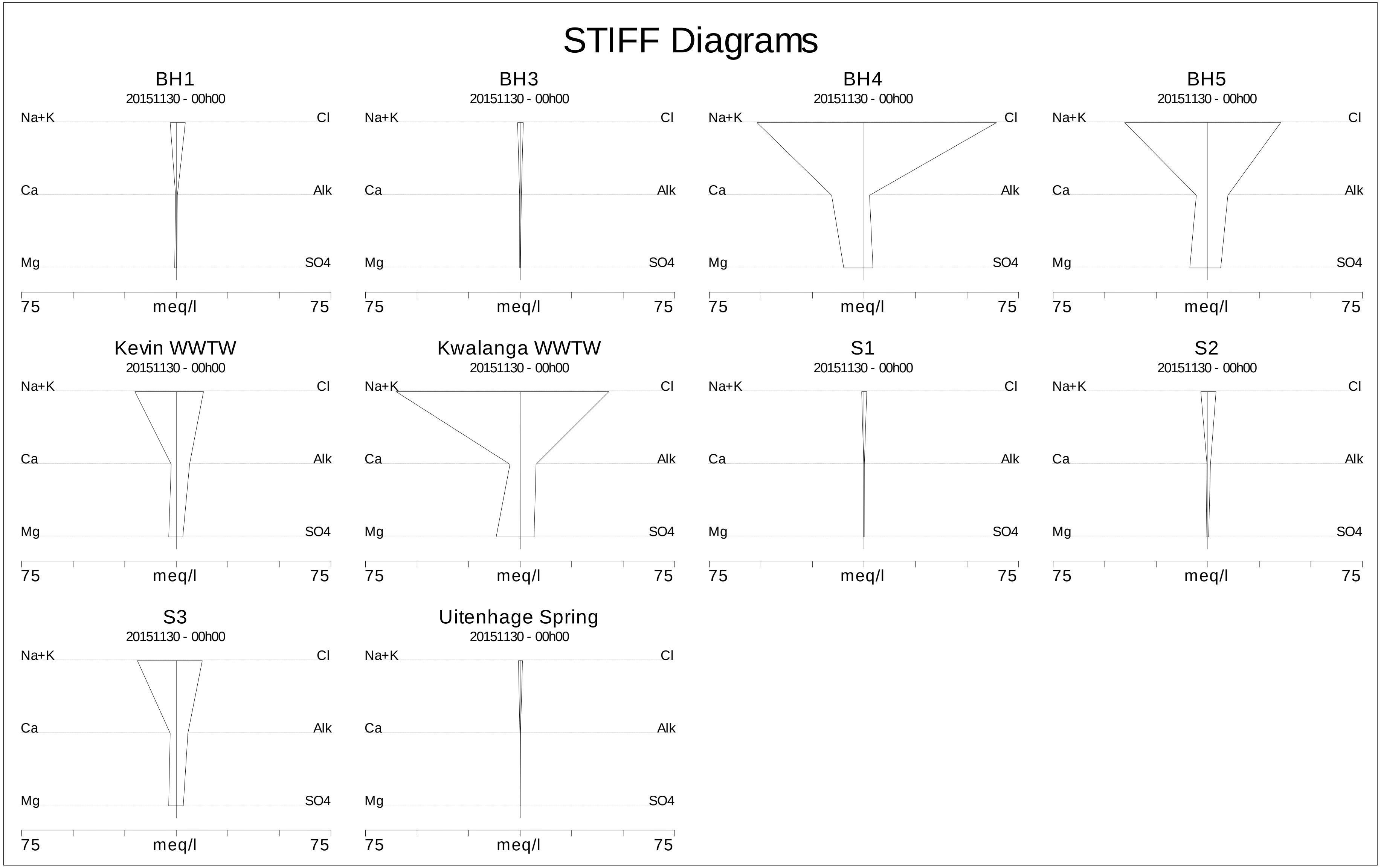

Figure 27 : Stiff Diagrams of the Uitenhage Water Sample

6.3 Metals

The concentrations of metals were investigated in the study area in November 2015 and January 2016 (Table 4) in order to determine the possible link between concentration of trace metals that are within the upper soil surface and the concentration of the trace metal observed in groundwater samples through percolation.

The concentrations of Pb in surface water samples in the November month from site S1 was 13.24 ppb, S2 was 9.17 ppb and S3 was 6.13 ppb. The concentration of Pb from a groundwater samples in the month of November from sites BH4 was 2.28 ppb, BH3 was 0 ppb, BH1 was 4.4 ppb and BH5 was 3.74 ppb. The Pb concentration from the spring was 71.48 ppb. According to South African National Standards (SANS 241-1: 2011) the acceptable limit for Pb was 26.0 ppb. This means that all the surface water and groundwater points were within the limit except for the water sample obtained from the Uitenhage spring. The Uitenhage spring might be directly fed from deep groundwater circulation that has passed through geological layers with a high content of Pb, which results to water from deep aquifer containing higher concentrations of Pb. The results for Pb from the surface water samples S1, S2, and S3 were 13.24 ppb, 9.17 ppb and 6.13 ppb, respectively. The depreciation of the concentration of Pb from upstream (S1) to downstream (S3) could be associated with dilution of highly concentrated water from upstream by stream water further downstream. The groundwater samples indicated the concentrations of 4.4 ppb, 0 ppb, 2.28 ppb and 3.74 ppb for Pb from BH1, BH3, BH4 and BH5, respectively; which were low concentrations as compared to surface water samples. This could be associated with the leaching from rocks, given the fact that the streamflow is recharged by water emanating from the mountains. In addition, the source of Pb could be the farming in areas surrounding S1, i.e. Pb might be emanating from the fertilisers (phosphate fertilizers and micronutrient fertilizers). The groundwater resource is protected from the runoff that comes with a high concentration of Pb from the farmer’s fields in the vicinity of S1 and that is the reason why the groundwater samples have the low concentrations of Pb.

The concentration of Cu and Cd was zero for both groundwater and surface water samples as there are no known sources of pollution that contain these particular elements. The vivid variation of surface and groundwater concentrations of Pb was a clear indication of a limited interaction between groundwater water and surface water resource. However, Cu from BH1 had high concentration (46.83 ppb), which was way above the SANS 241-1: 2011 limits. Furthermore, this was an outlier, which its concentration could not be associated with any activity on site and it could not be associated with local geology of the area either.

The concentration of Pb in surface water samples in the month of January from site S1 was 11.02 ppb, S2 was 9.42 ppb and S3 was 15.59 ppb. The concentration of Pb from groundwater samples in the month of January from sites BH1 was 0 ppb, BH3 was 16.89 ppb, BH4 was 0 ppb, and BH5 was not analysed. The concentration of Pb from the spring was 26.18 ppb which was above the limit in terms of SANS 241-1: 2011. Even during the month of January the surface water points and groundwater points were within the limit, except for the water sample obtained from the Uitenhage spring. The reason for the high concentration of Pb in the Uitenhage spring was the same as the one cited during the month of November, and the reason was that the spring might be directly fed from deep groundwater circulation that has passed through geological layers with a high content of Pb, which results to water from deep aquifer containing higher concentrations of Pb. On average, the concentrations of Pb on the samples obtained in November 2015 was higher than that one of the concentrations obtained in January 2016 and the occurrence of rain in January was lower than the occurrence of rain in November (Figure 10 in chapter 3). The less concentration of Pb in January can be associated with the low occurrence of rain in the same month, which led to an ineffective transportation of Pb content for detection of high concentrations to the resources. Even during the month of January 2016, on average, the concentration of Pb from surface water samples remained higher than the concentration Pb in groundwater; this can still be used as an evidence for the limited interaction between groundwater and groundwater resources.

In month of January 2016, the concentration of Cd and Pb from spring water sample also exceeded acceptable standards. This was also probably due to deep groundwater circulation, which can be influenced by the underlying geology as a result of the long residence time or can be due to any influence of chemical factors. The concentration of Cd in BH3 and BH1, were 7.47 ppb and 4.99 ppb, respectively, which experienced high concentration of Cd in January 2016. The concentration of Cu in BH1 was 415 ppb, which also exceeded the limit. These high concentrations may be due to farming activities that contaminate subsurface recharge, which leaks into the boreholes. This could also be related to seasonal change. Furthermore, the aquifer maybe mineralised with high concentrations of Cu then other metals. The TMG aquifers contain impurity of pyrite as well as sulphide metals;   BH1 is at the outcrop TMG.

Table 4: Analytical results of the concentration of heavy metals for groundwater and surface water samples

Site ID	Date	Cadmium (ppb)	Lead (ppb)	Copper (ppb)	Date	Cadmium (ppb)	Lead (ppb)	Copper (ppb)
	Limit	**0.097**	**26.0**	**22.6**		**0.097**	**26.0**	**22.6**
Uitenhage Spring	Nov 2015	0	71.48	0	Jan 2016	11.31	26.18	0
S1	Nov 2015	0	13.24	0	Jan 2016	0	11.02	0
S2	Nov 2015	0	9.17	0	Jan 2016	0	9.42	0
S3	Nov 2015	0	6.13	0	Jan 2016	0	15.59	0
BH4	Nov 2015	0	2.28	0	Jan 2016	0	0	0
BH3	Nov 2015	0	0	0	Jan 2016	7.47	16.89	0
BH1	Nov 2015	0	4.4	46.83	Jan 2016	4.99	0	415
BH5	Nov 2015	0	3.74	0	Jan 2016	-	-	-

6.4 Bacteriological analysis.

Bacteriological culture was conducted to determine the link between the two water sources (surface water and groundwater). The distribution of different species for different water sources are presented in Figure 28 and Table 5. The wet season covers the months of November 2014 and January 2016 where as dry season covers the months of June 2015 and August 2015. Each bacteria count (MPN) is represented as MPN per 100ml. The negative (-) sign in the Table 5 indicates that there was no samples collected for the particular bacteria.

Wet season (November 2014 and January 2016)

During the wet season (November 2014**)**, the *E. Coli* count for surface water samples, S1, S2 and S3 were 56, 190 and 97 per 100ml of water, respectively. The *E. Coli* counts in the groundwater samples for the same month were read as 166/100ml in BH1, 150/100ml in BH2, 5/100ml in BH3 and 219/100ml in BH4. There were only 7 counts/100ml that were found for the Uitenhage spring water sample. Figure 28 shows *E. Coli* count at S2 was high when compared to S1 and S3; this might be due to factors such as sewage effluents from treatment works that are discharging directly into the Swartkops River at S2. The bacterial count in borehole samples from BH1, BH4 and BH2 were found to be high as compared to BH3, however, BH4 had high number as compared to surface water samples. In the Uitenhage spring, low counts were noted as compared to surface water and groundwater samples, except that of BH3. The high counts on groundwater could be associated with surface runoff rich pesticides controls and fertilizers, which percolates into the aquifer and eventually leaks into boreholes. The high counts in groundwater can also be an indication of the recent contamination, which is due high water table that occurred during the wet season. Furthermore, it could also be associated with other farming activities that were occurring in that area during that season.

The Enterobacter Aerogens (E. Aerogens) in Swartkops River was 53/100ml at S1, whilst none found at S2 and S3. In addition to the E. Aerogens living in water, it can also be found in the soil. The E. Aerogens found at S1 maybe from the soil in that area, which probably has a structure favouring their survival other than the soils structures found at S2 and S3. This could also be due to dilution when bacteria enter the river and mix with a high volume of freshwater. The bacterial counts in November 2014 for groundwater samples were 92/100ml, 0/100ml, 32/100ml, 51/100ml, for BH1, BH2, BH3 and BH4, respectively. The counts were high in BH1 as compared to other groundwater samples as well as surface water samples. This could be possibly due to land based activities such as farming activities and surface runoff during this season, as a results of high rainfall and irrigation flows as well as differing soil structures as indicated above. In the spring water sample, there was no microbial detected, which probably indicates that the spring water emanated from deep groundwater circulation. Unfortunately, the Proteus Mirabilis bacteria was not analysed for the month of November 2014.

In January 2016, *E. Coli* was not detected in both surface water and groundwater, except in the Uitenhage spring; only one count was detected in the spring. Although this was a rainy season, the flows were very low as a result of drought; the low counts of the *E. Coli* bacteria indicated that the wastewater discharge was free of this bacteria. The E. Aerogens from the surface water samples the counts were 2/100ml, 35/100ml, and 17/100ml for S1, S2 and S3 respectively. More bacterial counts were noted in S2 followed by S3. The high counts were probably due to other land base activities such farming activities. The bacterial count at WWTW – Kwalanga and WWTW- Kevin were read as 0 and 2, respectively. The groundwater samples also had low counts that were noted as 1/100ml in BH1, 1/100ml in BH3 and 0/100ml in BH4. This low bacterial count was probably due to low rainfall during the month of January that is related to low runoff which was associated with year 2015/2016 drought. In the Uitenhage spring, the E. Aerogens counts were high (80/100ml) as compared to surface water and other groundwater samples. This value seems to be related to surface contamination. Given the fact that during the sampling period there was low rainfall received which could have transported contaminants into the spring through surface runoff.

Proteus Mirabilis (P. Mirabilis) in the month of January 2016, S1 were read as 200/100ml; S2 as 4/100ml and S3 as 61/100ml. The WWTW – Kwalanga and WWTW - Kevin were read as 7/100ml and 150/100ml, respectively. The counts in groundwater for BH1 were 32/100ml, 50/100ml for BH3 and 180/100ml for BH4. The counts at S2 were very low as compare to S1 and S3. This is probably due to damming effect at S2, which reduces the concentration of bacterial. The high counts at S3 might be due to Kevin WWTW that is discharging between S2 and S3. This may be due to improper function of the treatment (WWTW) plant. In contrary, the counts were low at Kwalanga, which could be as a result of well-functioning of the WWTW. The P. Mirabilis was high (180/100ml) at BH4 as compared to BH3 and BH1. There could be many factors that can be associated with this high value as previously shown by hydrochemistry results in section 6.2. Besides the chicken farm that is located within the vicinity of this borehole, there could be other unknown anthropogenic activities that could be generating various contaminants which end-up in groundwater.

Dry season (April to September)

In June 2015, the *E. Coli* was observed to be 19/100ml at S1, 12/100ml at S2 and 7/100ml at S3. It is more likely that the high count of *E. Coli* in S1 maybe runoff as a result of winter rainfall and defecation, which is related to poor sanitation. The *E. Coli* was observed to be low at S3 as compared to S2. This difference in microbial community may be due to human settlement found in the area. There was no *E. Coli* detected in groundwater samples except in BH4, where one count was found. The Uitenhage spring also no bacteria were detected.

E. Aerogens in surface water were 9/100ml at S1, 1/100ml at S2 and 74/100ml at S3. The counts in groundwater were 1/100ml at BH1, 0/100ml at BH3 and 18/100ml at BH4. In the Uitenhage spring only one (1/100ml) count was observed. The S3 counts were high than S1 and S2, this possibly due to discharge from WWTWs that are discharging directly into the river between S2 and S3. The low counts in groundwater were observed and was probably due to seasonal change, except that of BH4, which was relatively high. As it was stated above at the vicinity of BH4 there could be other unknown anthropogenic activities that could be generating various contaminants which end-up in groundwater. It was possible that the relatively high count that month resulted from those unknown activities.

In June 2015 month, the observation of the P. Mirabilis counts from surface water samples were 0 at S1, 41 at S2 and 39 at S3. It might again be due to WWTWs discharging into stream between S2 and S3 as stated above. The bacterial counts in groundwater were 1 at BH1, 70 at BH3, 24 at BH4 and 9 at Uitenhage Spring. The high counts in BH3 and BH4 were possibly as a result of seasonal change and/or land base activities in farms.

The *E. Coli* counts were not found in samples collect in August 2015, except for S2 and BH5 (Table 4), which were 5 for 3 respectively. The counts of E. Aerogens also behave similar as for the *E. Coli* for this period, again there were only found at S2 and BH5, which were 26 and 13 respectively. This again could be as a result of seasonal change.

The counts on P. Mirabilis for surface water samples were 7/100ml for S1, 44/100ml for S2 and 0/100ml for S3. The groundwater samples were 0/100ml for BH1, 12/100ml for BH3, 8/100ml for BH5 and 0/100ml for Uitenhage spring. The high counts on S2 were probably due to discharge of the WWTW (Kwalanga) that was discharging into the river at S2. The counts found in groundwater were probably due to land base activities and seasonal changes.

Overall, the results of the bacteriological counts indicated the evidence of limited interaction between the two sources (groundwater and surface water); there was good correlation between surface water (S2) and groundwater (BH5) in August 2015. However, it should be noted that the sample for BH5 was only collected in August 2015. Except BH5, all the other boreholes are located on the other side of the fault (Coega Ridge Aquifer). This was expected when taking into account the groundwater flow gradient. According to the groundwater water flow direction (Figure 12 and Figure 21), the fault that divides two aquifers acts as a pathway for groundwater flow, however, pollutants cannot migrate from Swartkops Aquifer to Coega Artesian Aquifer where most of the boreholes are located. The groundwater does flow through the fault from Coega Artesian Aquifer to Swartkops Aquifer. It appeared that the Coega Artesian Aquifer was not vulnerable to the polluting activities taking place in the vicinity of Swartkops Aquifer.

Figure 28 depicts high bacterial count during the wet season (November 2014 and January 2016) as compared to dry season (June 2015 and August 2015). The pollutants were transported through runoff to the aquifers. This was an indication that both aquifers were vulnerable to pollution that emanates from land base activities (such as industrial waste, discharge from WWTWs and farming activities).

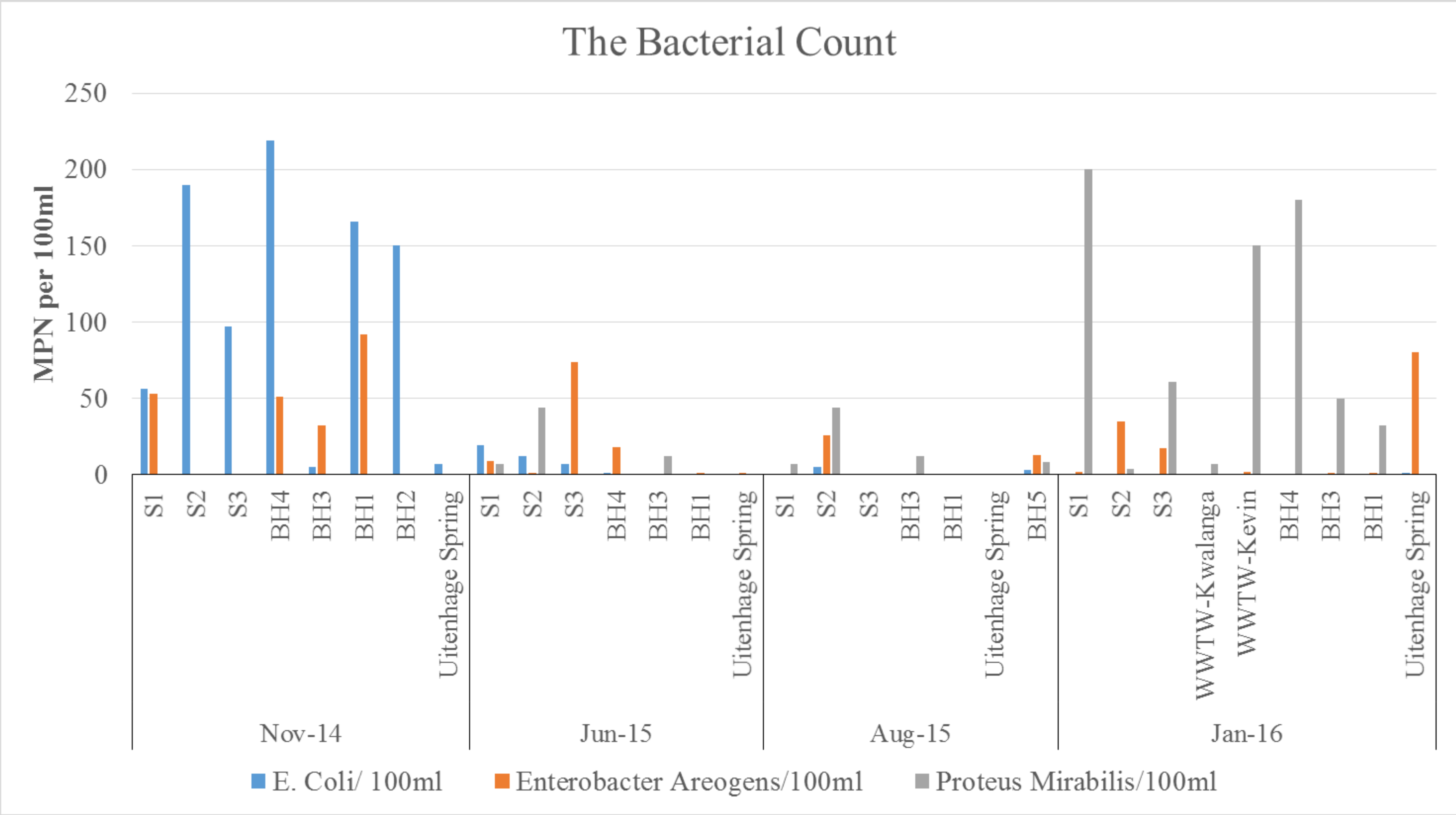

Figure 28: showing the bacterial count for different observation periods

Table 5: Bacteria Analyses

Sample	Date	E. Coli/ 100ml	Enterobacter Areogens/100ml	Date	E. Coli/ 100ml	Enterobacter Areogens/100ml	Proteus Mirabilis/100ml	Date	E. Coli/ 100ml	Enterobacter Areogens/100ml	Proteus Mirabilis/100ml	Date	E. Coli/ 100ml	Enterobacter Areogens/100ml	Proteus Mirabilis/100ml
S1	Nov 2014	56	53	Jun 2015	19	9	0	Aug 2015	0	0	7	Jan 2016	0	2	200
S2	Nov 2014	190	0	Jun 2015	12	1	41	Aug 2015	5	26	44	Jan 2016	0	35	4
S3	Nov 2014	97	0	Jun 2015	7	74	39	Aug 2015	0	0	0	Jan 2016	0	17	61
WWTW-Kwalanga	Nov 2014	-	-	Jun 2015	-	-	-	Aug 2015	-	-	-	Jan 2016	0	0	150
WWTW-Kevin	Nov 2014	-	-	Jun 2015	-	-	-	Aug 2015	-	-	-	Jan 2016	0	2	7
BH1	Nov 2014	166	92	Jun 2015	0	1	1	Aug 2015	0	0	0	Jan 2016	0	1	32
BH2	Nov 2014	150	0	Jun 2015	-	-	-	Aug 2015	-	-	-	Jan 2016	-	-	-
BH3	Nov 2014	5	32	Jun 2015	0	0	70	Aug 2015	0	0	12	Jan 2016	0	1	50
BH4	Nov 2014	219	51	Jun 2015	1	18	24	Aug 2015	-	-	-	Jan 2016	0	0	180
BH5	Nov 2014	-	-	Jun 2015	-	-	-	Aug 2015	3	13	8	Jan 2016	-	-	-
Uitenhage Spring	Nov 2014	7	0	Jun 2015	0	1	9	Aug 2015	0	0	0	Jan 2016	1	80	0

6.5 Conceptual hydrogeological model

From the integration of geological, structural, hydrostratigraphic units and groundwater flow investigation, a probable hydrogeological conceptual model for the area has been constructed.

Figure 29 shows the schematic hydrogeological conceptual model a, which represent aquifer configuration in the area. It also shows the structural control and an envisaged groundwater circulation in the main aquifers identified in the area.

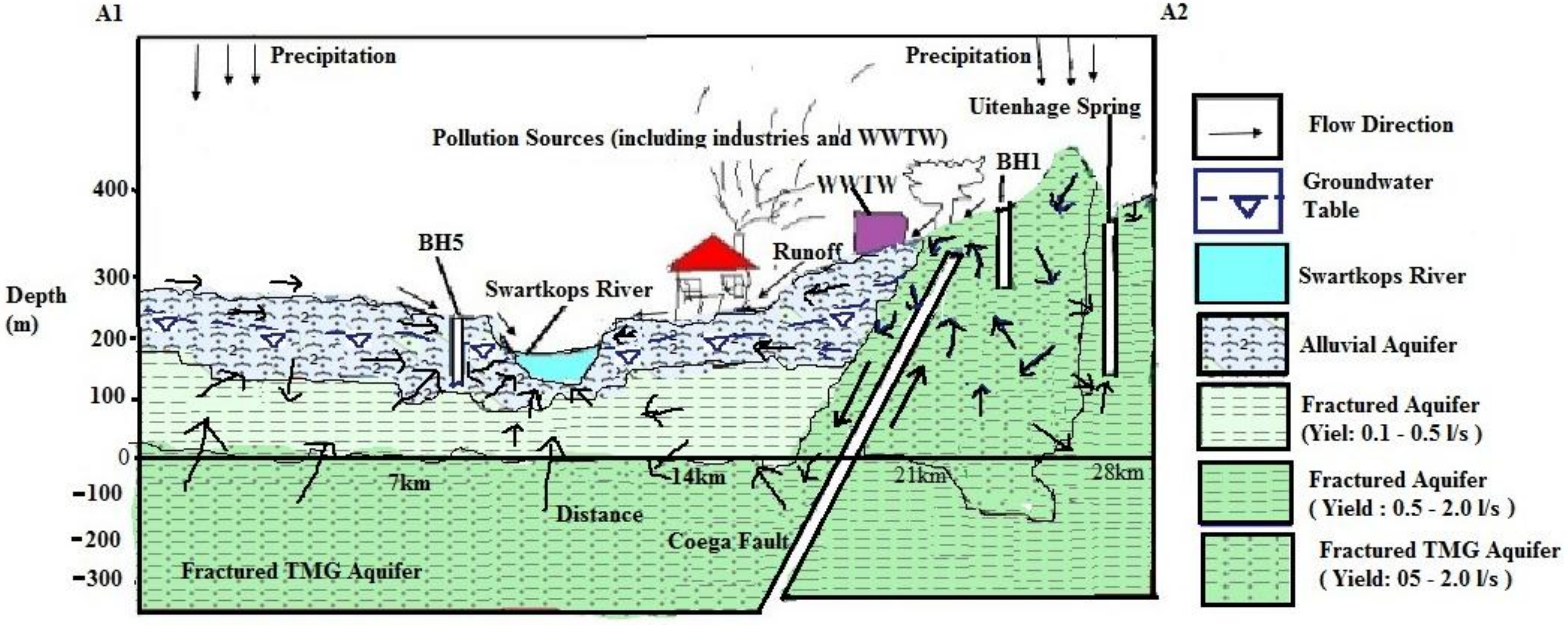

Figure 29: Schematic hydrogeological conceptual model

Based on the schematic groundwater conceptual model (Figure 29) and analyses of the results indicated that the Swartkops River was gaining water from the groundwater.

The pollutants in the study area are probably due to WWTW, industrial waste and agricultural waste, which are all situated in the Swartkops Aquifer. In the Coega Aquifer there is an imperative spring, which is in the Government Water Controlled Area (GWCA); the area is impact free. Therefore, the Coega Ridge Aquifer is unlikely to negatively affect the Swartkops Aquifer even though groundwater flows across the fault.

7. CHAPTER SEVEN: CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

Integrated method was applied in order to achieve the set objectives. The Bayesian interpolation method resulted a strong correlation between the groundwater level elevation surface topography for shallow aquifer.

Groundwater flows towards the direction of the surface topography. Both groundwater and surface water are draining towards east direction to the Indian Ocean through Blue Water Bay. The fault that divides the two aquifers (Swartkops and Coega Ridge Aquifers) is permeable (has no impact on groundwater circulation) and act as a pathway for migration of groundwater pollutants and due to different hydraulic gradient, groundwater only flow from Coega Ridge Aquifer to Swartkops Aquifer. Based on the groundwater flow gradient, it was observed that Coega Rigde Aquifer is not vulnerable to pollution from Swartkops Aquifer. It should be noted that the Coega Ridge aquifer is a Government Water Controlled Area; as a result, the flows from the Coega Ridge Aquifer were not expected to have an influence on the Swartkops Aquifer.

The stable isotopes data also revealed that during the winter season the $\delta^{18}O$ and $\delta^{2}H$ signature indicated the depletion, which was greater at low temperature, i.e. $\delta^{18}O$ values are more negative in winter. The groundwater samples revealed deep groundwater circulation as well as seasonal changes. The surface water samples were more enriched with heavy isotopes as compared to groundwater samples as a result of evaporation process and waste water return. The results also indicated that the isotopic composition of groundwater from borehole BH5 was related to the Swartkops River water samples, and hence an evidence for the mixing process. The stable isotope signatures of BH5 and Swartkops River are indicated that groundwater and groundwater interaction. The tritium results also concur with the stable isotopes of $\delta^{18}O$ and $\delta^{2}H$. Due to the influence of the fault the Swartkops River did not have an influence on the other aquifer, hence no interaction established between the Swartkops River samples and the boreholes located on Coega Aquifer.

Based on the Piper diagram, the dominant facies of water is Na-Cl type, which is typical deep circulating water. However, the other water sample collected in winter (June 2015) from BH4 indicated Ca-Cl water type, typical of mine water environment. This was an indication of longer residence time that results to higher degree of ion exchange, which also results to higher salinity in the groundwater. The study revealed that the sources of pollution were farming activities, municipal waste water as well as industries. The results observed from the piper diagram and Stiff diagram were also supported by the results observed from trace metals. The results also indicated the limited interaction, only noticeable in the BH5. The lack of evidence of interaction between Swartkops River and other boreholes could be due to flow gradient between the two aquifers.

The distribution of microbials indicated the evidence of limited interaction between the two sources (groundwater and surface water); there is good correlation between surface water, which concurs with all other analysis stated above.

Overall, there is an interaction between surface water and groundwater, as a result, the fault act as a pathway for groundwater flow between the two aquifers and a result of flow gradient and the pollution from Swartkops Aquifer is unlikely to impact the Coega Aquifer. Therefore, the Swartkops Aquifer is vulnerable to pollution from Swartkops River. Although the Coega Aquifer is not vulnerable to Swartkops River pollution, however, it can be impacted by minimal pollutants from farming activities.

7.2 Recommendations

- Ideally, it would be preferable to have boreholes in the close proximity of the three sampling points along the river.
- Water quality monitoring boreholes need to be drilled, specifically for water quality as suggested by Venables, 1985.

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9. Appendix A: Water Quality

Table 6: Laboratory chemical analysis results of water quality samples.

Sample Date	Site ID	Total Dissolved Solids (mg/L)	Nitrate NO_3 as N (mg/L)	Chlorides as C l(mg/L)	Total Alkalinity as $CaCO_3$ (mg/L)	Sulphate as SO_4 (mg/L)	Calcium as Ca (mg/L)	Magnesium as Mg (mg/L)	Sodium as Na (mg/L)	Potassium as K (mg/L)	Conductivity at 25° C (mS/m)	pH-Value at 25° C
	Class I: (Recommended)	<1000	<10	<200	N/S	<400	<150	<70	<200	<50	<150	5-9.5
	Class II:(Max. Allowable)	1000-2400	20-Oct	200-600	N/S	400-600	150-300	70-100	200-400	50-100	150-370	4-5 or 9.5-10
Nov. 2014	BH3	151.2	-0.1	37.4	29.3	7	5.5	3.4	-0.1	-0.02	21.6	6.7
Nov. 2014	BH4	9814	-0.1	4894.5	162	369.1	690.4	162.1	0.25	-0.02	1402	7.5
Nov. 2014	BH2	145.6	-0.1	35.9	27.6	6.1	4.3	2.5	-0.1	-0.02	20.8	6.5
Nov. 2014	BH1	249.9	0.25	86.3	26.9	8.4	5	4.9	-0.1	0.14	35.7	6.3
Nov. 2014	Uitenhage Spring	95.2	0.14	32.9	-10	-3	2.5	1.9	-0.1	0.04	13.6	5.2
Nov. 2014	S1	149.1	0.3	44.2	10.5	7.1	3.8	2.6	-0.1	-0.02	21.3	7
Nov. 2014	S2	879.9	0.97	251.6	120	48.6	22.3	21.8	0.55	0.12	125.7	7.6
Feb. 2015	BH3	148.4	-0.1	39.3	25.5	8.4	4.1	3.3	-0.1	0.02	21.2	6.6
Feb. 2015	BH4	8946	0.27	1355.3	184.2	355.4	565.2	149.6	0.21	-0.02	1278	7.8
Feb. 2015	BH2	147	-0.1	37.2	33.8	6.1	5.4	2.9	-0.1	0.02	21	6.6
Feb. 2015	BH1	252	0.43	79.1	24.9	9.5	3.4	3.9	-0.1	0.15	36	6.2
Feb. 2015	Uitenhage Spring	97.3	0.14	34	-10	2.8	-2.5	1.9	-0.1	0.03	13.9	4.9
Feb. 2015	S1	134.4	-0.1	45.1	15.2	3.4	-2.5	3.1	-0.1	-0.02	19.2	7.2
Feb. 2015	S2	1364.3	1.74	453.5	195.7	78.5	32.1	36.1	1.43	0.18	194.9	8
Feb. 2015	S3	1232.7	3.21	336	220.7	123.9	36.5	28.5	0.19	3.25	176.1	8.1
Jun. 2015	BH4	8562.6	0.27	1355.3	184.2	355.4	565.2	149.6	16	78	1278	7.8

Sample Date	Site ID	Total Dissolved Solids (mg/L)	Nitrate NO_3 as N (mg/L)	Chlorides as Cl (mg/L)	Total Alkalinity as $CaCO_3$ (mg/L)	Sulphate as SO_4 (mg/L)	Calcium as Ca (mg/L)	Magnesium as Mg (mg/L)	Sodium as Na (mg/L)	Potassium as K (mg/L)	Conductivity at 25° C (mS/m)	pH-Value at 25° C
	Class I: (Recommended)	<1000	<10	<200	N/S	<400	<150	<70	<200	<50	<150	5-9.5
	Class II:(Max. Allowable)	1000-2400	20-Oct	200-600	N/S	400-600	150-300	70-100	200-400	50-100	150-370	4-5 or 9.5-10
Jun. 2015	BH3	140.7	-0.1	37.9	26.4	6	5.7	3.2	22.1	7.3	21	6.9
Jun. 2015	Uitenhage Spring	95.14	0.14	34.6	-10	3.1	4.1	1.8	16.9	-1	14.2	5.7
Jun. 2015	BH1	244.55	0.44	83.3	21.5	9.4	5.3	6.1	52.2	1.2	36.5	6.6
Jun. 2015	S1	119.93	-0.1	41.4	-10	5.1	4	2.6	23	-1	17.9	6.9
Jun. 2015	S2	1449.21	2.91	469.2	146.3	112.5	47.5	44.5	645	16	216.3	8.1
Jun. 2015	S3	1564.45	1.5	488.3	258	170.1	53.7	38	575	23.3	233.5	8.2
Aug. 2015	BH1	728.96	0.55	288.3	28.5	19.3	18	25.6	152.7	1.6	108.8	6.3
Aug. 2015	S1	101.84	-0.1	33.4	-10	4.9	-2.5	1.9	24	-1	15.2	6.6
Aug. 2015	S2	394.63	0.51	127.1	41.6	30	8.4	10.5	89.4	4.3	58.9	7.4
Aug. 2015	S3	1836.47	1.98	483	306.5	181.4	55	46.8	420.2	26.9	274.1	8.1
Aug. 2015	BH3	144.05	-0.1	35.6	34.5	5.6	5.7	2.6	25.9	7	21.5	6.7
Aug. 2015	BH5	2974.8	14.57	1229.1	440.1	267.3	96.3	84.2	809.9	22.3	444	7.8
Aug. 2015	Uitenhage Spring	91.12	0.14	32	-10	3.8	-2.5	-1.5	20.9	-1	13.6	5.3
Nov. 2015	BH1	1583.21	0.42	155	26.4	11.9	7	9.6	66.5	-2.5	236.3	8.3
Nov. 2015	S1	115.91	0.34	47.6	-10	6.3	-2.5	2.4	24.6	-2.5	17.3	6.7
Nov. 2015	S2	3403.6	0.1	141.7	65.1	21	8.3	9.9	76	-2.5	508	8.2

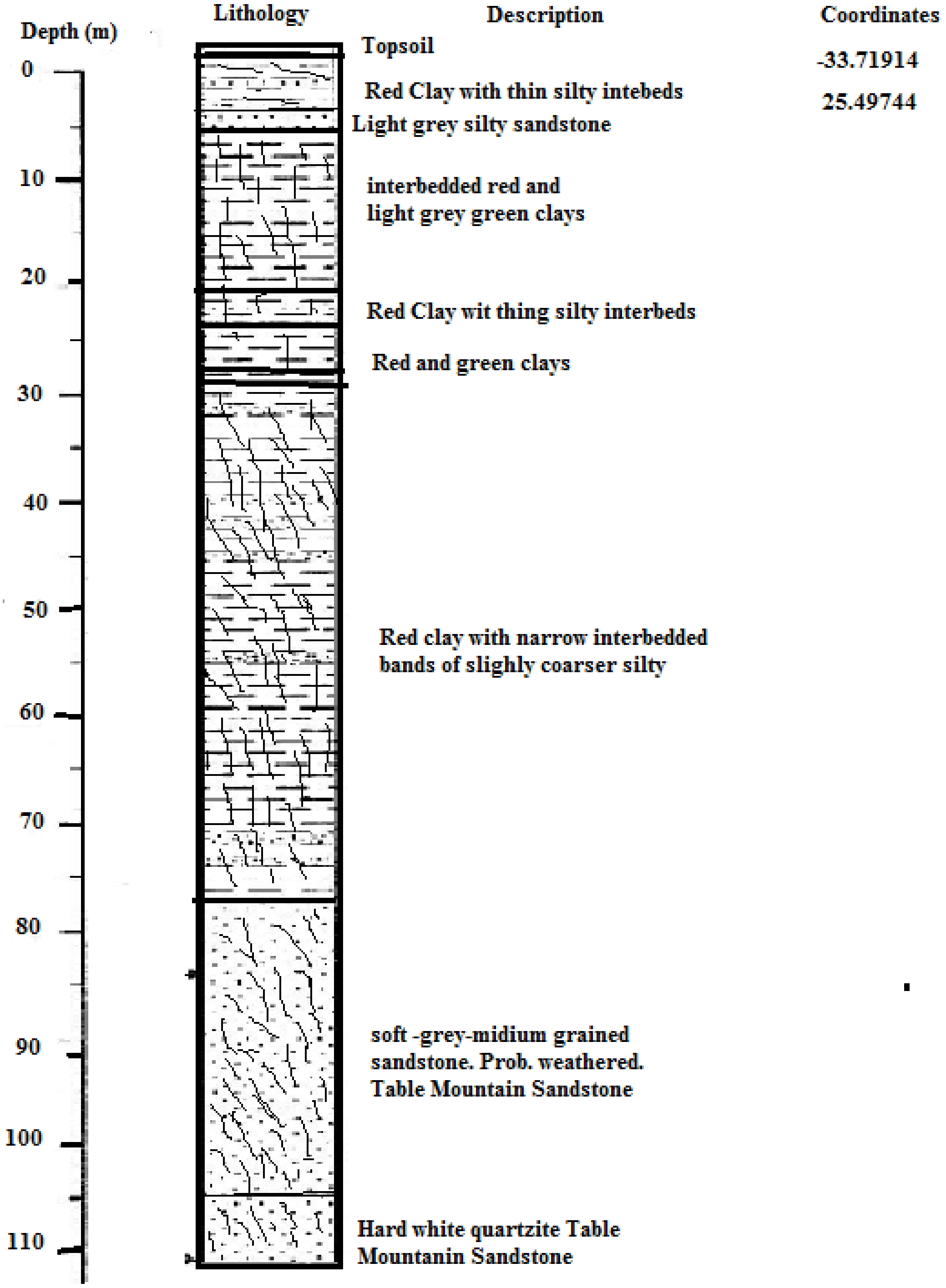
Sample Date	Site ID	Total Dissolved Solids (mg/L)	Nitrate NO_3 as N (mg/L)	Chlorides as C l(mg/L)	Total Alkalinity as $CaCO_3$ (mg/L)	Sulphate as SO_4 (mg/L)	Calcium as Ca (mg/L)	Magnesium as Mg (mg/L)	Sodium as Na (mg/L)	Potassium as K (mg/L)	Conductivity at 25° C (mS/m)	pH-Value at 25° C
	Class I: (Recommended)	<1000	<10	<200	N/S	<400	<150	<70	<200	<50	<150	5-9.5
	Class II:(Max. Allowable)	1000-2400	20-Oct	200-600	N/S	400-600	150-300	70-100	200-400	50-100	150-370	4-5 or 9.5-10
Nov. 2015	S3	326.29	0.53	445.8	281.3	163.4	59.5	45	419.7	24.1	48.7	7.2
Nov. 2015	BH3	144.05	-0.1	55.3	29.7	8.3	5.2	2.8	24.8	6.6	21.5	7.9
Nov. 2015	BH5	366.49	13.79	1217.6	487.3	301.5	111.8	106.4	912.5	24.9	54.7	8.1
Nov. 2015	Uitenhage Spring	91.12	0.17	41.1	-10	3.3	-2.5	-1.5	18	-2.5	13.6	6
Nov. 2015	BH4	4917.8	0.11	2275.5	135.9	209.8	314.1	119.1	1181.7	17.2	734	7.3
Nov. 2015	WWTW Kwalanga	3832.4	9.82	1499.9	386.1	325.7	99.2	141.2	1359.2	40.3	572	9
Nov. 2015	WWTW Kevin	1628.77	0.27	467	321.9	152.4	49.8	44.7	447	25	243.1	8.3

10. Appendix B: Borehole Logs

BH3 -Private Borehole (Venables, 1985).

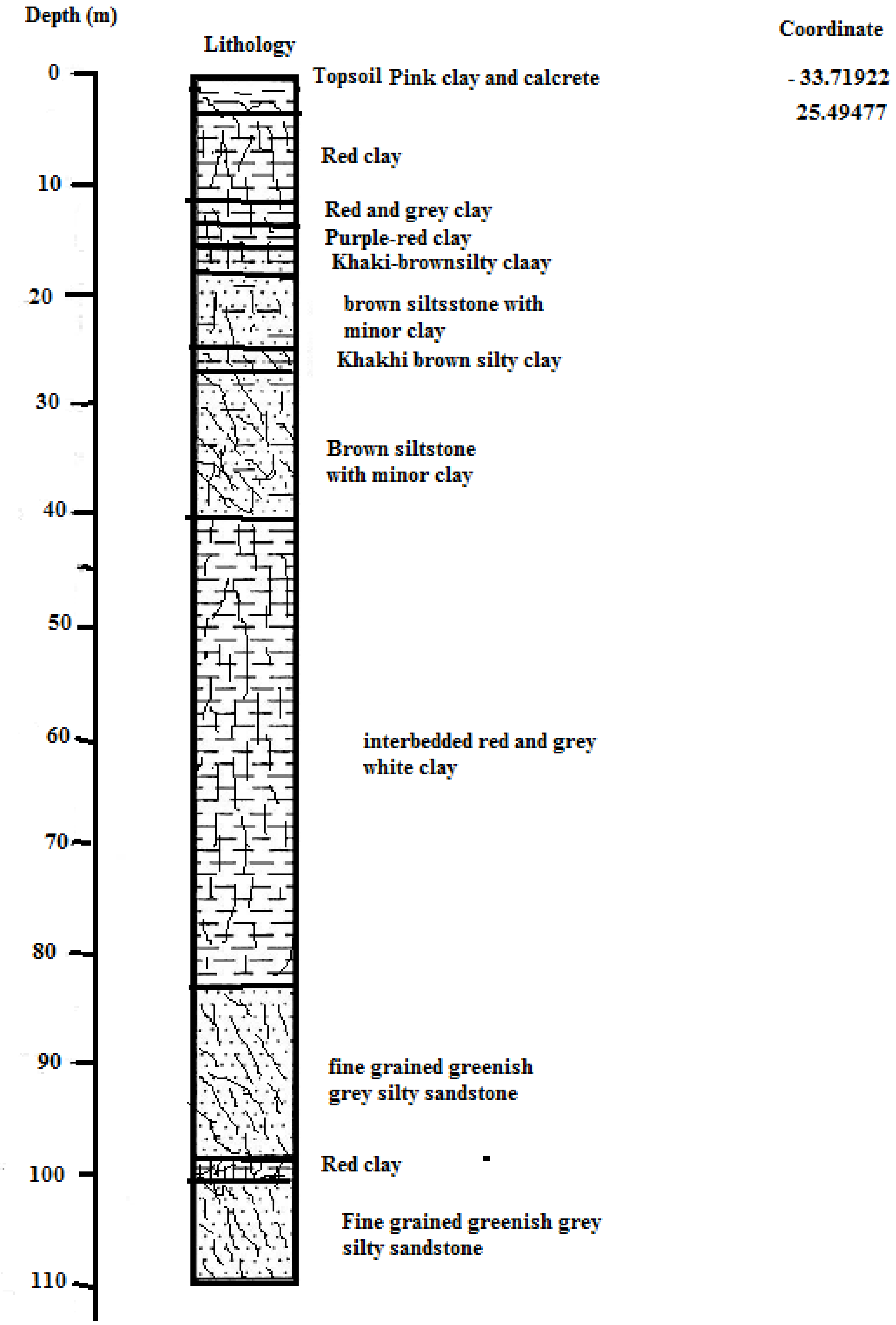
Cadastral farm: Sovereign Foods

Yield:~7.7 l/sec



BH4 -Private Borehole (Venables, 1985)

Cadastral farm: Sovereign Foods at Rietheuwel



11. Appendix C: This paper was presented at the groundwater development conference for input.

A STUDY OF INTERACTION BETWEEN GROUNDWATER AND SURFACE WATER USING ENVIRONMENTAL ISOTOPES, HYDROCHEMISTRY AND FEACAL COLIFORM BACTERIA IN THE UITENHAGE BASIN, EASTERN CAPE

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1. Abstract

The Table Mountain Group (TMG) Formation in the Uitenhage region, in the Eastern Cape Province of South Africa, has many groundwater users, which could result in the over-exploitation of the underlying aquifer. Consequently, several investigations have been conducted to help in the planning and management of groundwater resources within the region. Traditionally, these investigations have considered groundwater and surface water as separate entities, and have been investigated separately. Environmental isotopes, hydrochemistry and faecal colifom bacteria techniques have proved to be useful in the formulation of interrelationships and for the understanding of groundwater and surface water interaction. The field survey and sampling of the springs, Swartkops River and the surrounding boreholes in the Uitenhage area have been conducted. After full analysis of the study, it is anticipated that the data from the spring, Swartkops River and the surrounding boreholes show interannual variation in the isotope values, indicating large variation in the degree of mixing, as well as to determine the origin and circulation time of different water bodies. Isotopes δD and $\delta^{18}O$ values for the spring ranges from −23.80‰ to −17.43‰, and 5.25‰ to 4.62‰, respectively, while δD values for borehole samples range from −27.50‰ to −19.10‰ and $\delta^{18}O$ values range from −5.67‰ to −4.49‰. In the river sample, δD values ranges from −17.70‰ to −4.18‰, $\delta^{18}O$ from −3.43‰ to −1.13‰, respectively. The chemical analyses results of groups of water samples from various localities in the TMG aquifer, the classification of the water type is that dominated by Na-Cl water which is typical old marine water. However, the sample from Sovereign Foods at Rietheuwel indicated Ca-Cl water type, typical of mine water environment. Its electrical conductivity (EC) is 1278 mS/m exceeding the limit of 150 mS/m, the maximum acceptable limit for domestic use. Swartkops River is an ephemeral, therefore it is expected that diffuse recharge occurs into the shallow aquifer. Therefore, the entrobacteraerogen and E.Coli bacteria were detected in the samples.

During wet season, the bacterial count downstream of the Swartkops River is high as compared to upstream, however there is very high count in the midstream and that may be due to lots of factors such as sewage effluents from treatment works. However, the bacterial count is vice versa during dry season. This could be due to dilution when bacteria enter the river and mix with a high volume of freshwater or the sewage systems management and treatment has been improved.

1.1 INTRODUCTION AND BACKGROUND

Winter *et al*. 1999, reported that, groundwater (GW) and surface water (SW) are two connected systems and by impacting the other, will eventually affect the other.

Despite the importance of the effeteness of the management of the water resource systems, the interactions groundwater/surface water systems are still less understood globally. Groundwater interacts with surface water features such as rivers, lakes, wetlands, estuaries and the sea through vertical and lateral flows. Over the past years, the main focus has been on studying and understanding the interactions between groundwater with rivers and lakes as these are the dominant entrance and exit points of surface and sub-surface interaction that are critical in terms of water resource management (Tanner, 2013).The relation between these two systems is in part influenced by climate (discharge volumes and patterns), geology, (aquifer properties and changes in topography), and cultural activity (like land-use, groundwater abstraction and the damming of rivers) (Lerner, 1996). Changes in these factors along the influence of a river will impact the relative elevation of the water table, and so dictate the type and extent of the groundwater/surface water interaction (Saayman et al. 2004).

Groundwater, surface water and springs are important source of water supply around Uitenhage area, and their protection is an essential part of hydrogeology. The water quality of these water bodies can differ depending on the location and environmental factors, such as the chemical composition of the underlying rocks, soil formations and the groundwater residence time (Aminiyan, *et al.,* 2016). This groundwater is susceptible to contamination from surface water (Swartkops River). If the groundwater pollutants were not detected for years, it becomes costly to remove them. Preventing the pollutants is less costly than removing contaminants from groundwater. Common types of contaminants include bacteria, viruses, and nitrates from irrigation. Moreover SWLR, 1995 and Quilbell et al., 1997; Jagals, et al., 1997 and Dallas and Day, 1993 reported the need for awareness to control the pollution.

Adequate understanding of groundwater and surface water interaction processes plays an important role in the planning of water abstractions from the boreholes. Given the fact that there are a vast number of groundwater users within the Table Mountain Group (TMG) region, it has resulted in many important investigations conducted to help in the planning and management of groundwater from the aquifer (Maclear, 2001). Predominantly, these investigations are vital in understanding groundwater and surface water interaction processes within the TMG aquifers. However, these processes remain poorly understood in the TMG region. Therefore, there is a gap in knowledge of the amount of groundwater usage, in relation to water abstraction licenses that are administered by the Department of Water and Sanitation (DWS).

Biological, hydrochemical and isotopic information can produce a practical management tool for groundwater resource. Patterns in biological, chemical and isotopic data are useful for fingerprint water sources and tracing flows and mixing processes in groundwater.

There are several methods of determining groundwater and surface water interaction for example, using pumping tests (Moench, 1995), tracer tests (Kalbus et al, 2006), and environmental tracer methods (Coplen *et al*., 2000; Hinkle *et al*., 2001). Amongst the above listed methods, the environmental tracer method (stable isotopes of oxygen and hydrogen, and radioactive isotopes of tritium, hydrochemistry) and feacal coliform bacteria have proved to be useful in understanding these interactions (Border, Winter, and Scarpino, 1978). All the methods available have their own advantages and disadvantages. It is therefore important to consider the objective of the study before a method is chosen. One of the advantages of using these methods is that they are relatively simple and cost effective.

This study is aimed at establishing an understanding of groundwater and surface water interactions of the TMG aquifers in Uitenhage area using environmental isotopes, hydrochemistry and feacal coliform bacteria. Environmental isotopes are employed worldwide in the groundwater and surface water studies, as they provide distinctive information on transport and interconnectivity of water resources (Abiye, 2013). The Interpretation of their chemical constituents in the water samples can provide an understanding in the stream aquifer connectivity.

2. STUDY AREA

The Uitenhage Aquifer is one of the well know artesian aquifers in South Africa. The study area covers about 211 km^2 (Figure 2). It is lying on the Swartkops River catchment just 38 kilometres north west of Port Elizabeth**.** The Uitenhage aquifer is occurring mostly within the Port Elizabeth and

Uitenhage Districts in the Eastern Cape Province of South Africa, and is recharged by rainfall on the Groot Winterhoek and Zunga Mountain ranges to the west (Maclear, 2001).The area lies within the primary Drainage Region M.

The Uitenhage Artesian Basin (UAB) is the most central artesian groundwater basin supplying water from springs for domestic use as well as supporting large citrus irrigation schemes in Uitenhage area. According to Maclear, 2001, groundwater from this basin was extensively utilised from the early part of the 21stcentury, including periods of over-exploitation that resulted in the declaration of a groundwater control area to limit abstraction to sustainable rates.

The UAB is separated by the Coega Fault into two aquifer systems, which are Coega Ridge Aquifer at the northern part of the Coega Fault and the relatively deep Swartkops Aquifer located at the southern part of the fault, as illustrated in Figure 1.

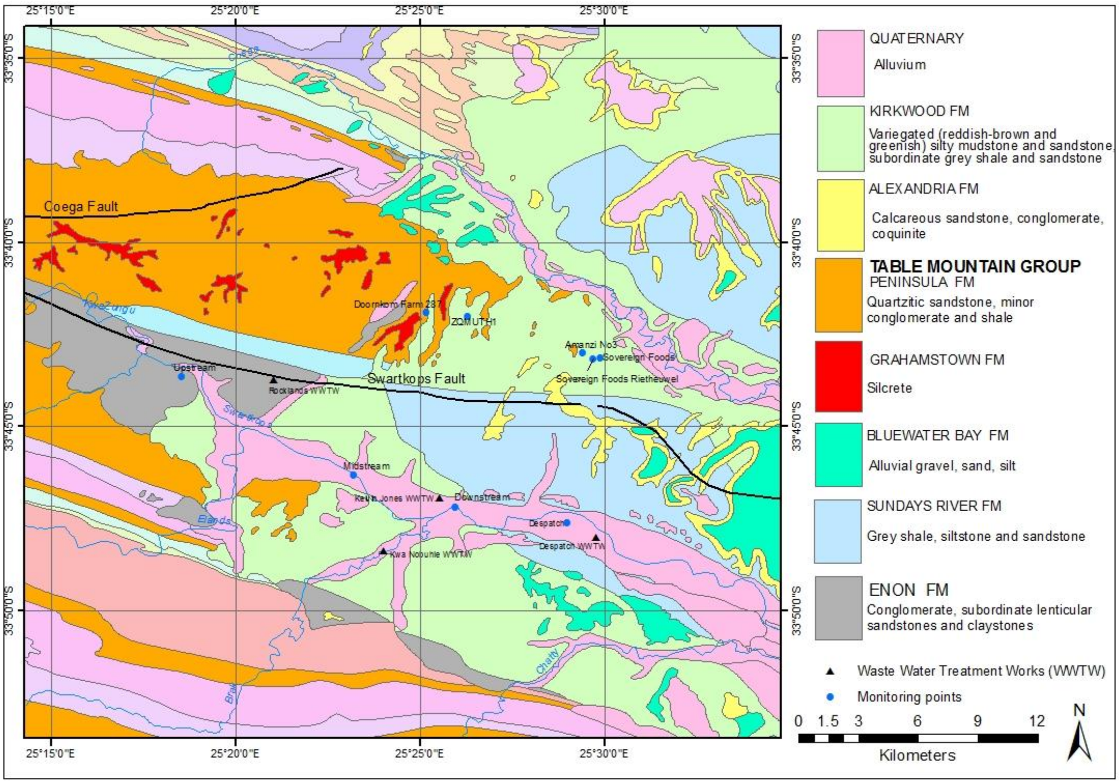

Figure 1: Map showing the locality of the study area

The Swartkops River is at the northern boundary of the Study Area, which extends from west to southeast eventually to the ocean at Blue Water Bay. They are potentially subjected to pollution from the industries located in the vicinity of the Swartkops River. Swartkop River Alluvial Aquifer occurs as a thin layer in the Swartkops Aquifer. According to Maclear, 2001 the two aquifers (Coega Ridge and Swartkops) have a similar hydrogeological conditions, with the difference is the depth. The Swartkops aquifer is relatively deeper as compared to Coega Aquifer.

2.1 GENERAL GEOLOGY

The geology and hydrological regime of groundwater characteristics are critical in assessment of the underlying aquifer systems as well as in planning for groundwater use. The aquifer comprises fractured TMG sandstones confined in the eastern part of the basin by overlying Cretaceous siltstones and mudstones, resulting in artesian conditions (Maclear, 2001). The western part of the Swartkops River catchment consists of the Groot Winterhoek Mountain and Kwazunga River valley, whilst the Elands and Van Stadens Mountain lies on the southern part. The Groot Winterhoek Mountain and Kwazunga River valley are characterized by the quartzitic sandstones of the TMG (Maclear, 1993, 2001). The eastern part of the Uitenhage basin is characterised mainly by Kirkwood, Quaternary and Sundays River Formation and some patches of the Alexander and Bluewater Bay Formation.

Figure 2 shows the monitoring boreholes that were drilled on the Uitenhage group (J-Ku), conglomerate, mudstone and sandstone covers relatively large area north of Port Elizabeth and south of the Suurberg and Klein Winterhoek Mountains. The Uitenhage and other older rocks are overlain by semi-consolidated calcareous sands and conglomerates of the Algoa Group (T-Qa) from Cannonvale towards Alexandria (Meyer, 1998).

Table 1: Shows the geological groups, subgroups, formations, thickness and reference.

Group	Subgroups	Formation	Thickness (m)	Reference
TMG		Basalt Sardinia Bay formation	180	Kent, (1980)
		Peninsula formation	1500	
		Cedarberg formation	50	
	Nardouw Subgroup		850	
Uitenhage Group		Basal Econ	3000	P.S Meyer October 1998
		Kirkwood	2200	
		Sundays River	1600	

2.2 HYDROGEOLOGY

The Uitenhage aquifer consists of the (TMG) sandstones, which are confined in the eastern part of the basin by Cretaceous siltstones and mudstones. This confinement causes the artesian conditions. Groundwater can be obtained from the discontinuous basal Alexandria conglomerate of the Algoa Group (P.S Meyer, 1998), the Uitenhage yield indicated to range between 0.1 *l/s* to > 5 *l/s.*

The competent quartzitic sandstones of the Table Mountain Group contain numerous faults, other fractures and joints, which can be targeted for groundwater development. According to Meyer (1998), the TMG yield indicated to range between 0.1 *l/s* to > 5 *l/s*.

The Department of Water and Sanitation (DWS) hydrogeological map (1:500 000 general hydrological map Port Elizabeth 3324) of the area indicates that the major portion of the study area is underlain by a fractured aquifer and borehole yields in the range of 0.1 ℓ/s to 0.5 ℓ/s. The aquifer yield is slightly higher (0.5 ℓ/s to 2.0 ℓ/s) in the vicinity of the Coega Fault.

The Table Mountain Group Aquifer occurs at significant depth and is protected by an aquiclude. However, it is an important aquifer to protect as it is high yielding and of ideal quality. The Table Mountain Group quartzitic sandstones are overlain by a thickness of post Palaeozoic sediments giving rise to artesian groundwater. There is an insignificant amount of groundwater abstraction from these deposits, mainly from areas along the Swartkops River.

3. METHODOLOGY

3.1 INTRODUCTION

Groundwater and surface water samples were collected from Uitenhage aquifer. There are eight water samples that were collected from November 2014, February 2015 and June 2015 for both isotopes, chemical and bacteriological analysis.

3.1.1 ISOTOPIC DATA AND LABORATORY ANALYSIS

The isotopes samples were collected using a 1-litre High Density Polyethylene (HDPE) bottles and immediately covered to avoid direct sunlight and were stored in a cooler box at 4^0C before being submitted to the isotope laboratory (iThemba Labs, Gauteng) for analysis. Water D/H ($^2H/^1H$) and $^{18}O/^{16}O$ ratios were analysed in the laboratory of the Environmental Isotope Group (EIG) of iThemba Laboratories, Gauteng. The equipment used for stable isotope analysis consists of a Thermo Delta V mass spectrometer connected to a Gas bench. Equilibration time for the water sample with hydrogen is about 40 minutes and CO_2 is equilibrated with a water sample in about twenty hours. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. The analytical precision is estimated at 0.2‰ for O and 0.8‰ for H.

3.1.2 CHEMICAL ANALYSES

The analyses of the chemical constituents were conducted as suggested standard methods by APHA (1995). The major ions like Ca, Mg, Na, K, Cl, SO4, NO3 and F were analyzed. The Ca and Mg were analyzed using titration with EDTA. Cl concentration in the samples was determined using Argentometric titration.

3.1.2 BACTERIOLOGICAL ANALYSIS

Water samples for bacteriological analysis were collected from November 2014, February 2015 and June 2015. These samples were analysed for enter-bacteria and *E. coli* using the Most Probable Number (MPN) technique (SABS). Results were expressed as MPN/100ml.

4. RESULTS AND DISCUSSION

4.1 INTRODUCTION

The variable of the hydrochemical and isotope analysis are essential components that indicate sources of water, recharge, residence time, and local geology without examining the geology. These variables can also assist in the investigation of groundwater and surface water interface. Groundwater and surface water can establish an integral part of a water cycle that can transport and spread contaminants from agricultural, industrial areas.

4.1.1ENVIRONMENTAL ISOTOPES

In order to evaluate the flow path regime of the local water resource, samples were submitted to the iThemba Laboratory of the Environmental Isotopes Group (EIG), Gauteng.

Table 2: Analytical Results of Environmental Radiogenic Tritium and Stable isotope Data.

Sample Identification	**Date**	**δ D (‰)**	**δ^{18}O (‰)**	**Tritium (T.U.)**	
Sovereign Foods	Nov. 2014	-20,28	-5,06	0,3	±0.2
Sovereign Foods Rietheuwel	Nov. 2014	-23,54	-5,25	0,0	±0.2
Amanzi 3	Nov. 2014	-21,30	-5,14	1,4	±0.3
Doornkom Farm 287	Nov. 2014	-19,10	-4,69	0,0	±0.2
Uitenhage Springs	Nov. 2014	-17,43	-4,82	0,0	±0.2
Swartkops River Upstream	Nov. 2014	-12,13	-3,17	1,4	±0.3
Swartkops River Midstream @ Bridge	Nov. 2014	-8,14	-2,12	1,2	±0.3
Sovereign Foods	Feb. 2015	-20,84	-5,44	0,3	±0.2
Sovereign Foods Rietheuwel	Feb. 2015	-22,76	-5,67	0,0	±0.2
Amanzi 3	Feb. 2015	-20,03	-5,16	0,2	±0.2
Doornkom Farm 287	Feb. 2015	-19,19	-4,69	1,1	±0.3
Uitenhage Springs	Feb. 2015	-18,90	-5,25	0,0	±0.2
Swartkops River Upstream	Feb. 2015	-6,38	-2,28	2,1	±0.3
Swartkops River Midstream @ Bridge	Feb. 2015	-4,18	-1,49	2,3	±0.3
Swartkops River Downstream @ Bridge	Feb. 2015	-4,45	-1,13	1,5	±0.3
Sovereign Foods	Jun. 2015	-25,90	-4,73	0,0	±0.2
Sovereign Foods Rietheuwel	Jun. 2015	-27,50	-4,96	0,6	±0.2
Doornkom Farm 287	Jun. 2015	-25,70	-4,49	0,5	±0.2
Uitenhage Springs	Jun. 2015	-23,80	-4,62	0,8	±0.2
Swartkops River Upstream	Jun. 2015	-17,70	-3,43	2,0	±0.3
Swartkops River Midstream @ Bridge	Jun. 2015	-11,50	-2,61	1,3	±0.3
Swartkops River Downstream @ Bridge	Jun. 2015	-15,9	-2,49	1,8	±0.3
Doornkom Farm 287	Aug. 2015	-18,5	-3,13	0,9	±0.3
Sovereign Foods	Aug. 2015	-19,4	-3,34	0,2	±0.2
Sovereign Foods Rietheuwel	Aug. 2015	-	-	-	-
Despatch	Aug. 2015	-12,8	-1,67	1,8	±0.3
Uitenhage Springs	Aug. 2015	-16,6	-2,81	0,0	±0.2
Swartkops River Upstream	Aug. 2015	-14,2	-2,66	1,4	±0.3
Swartkops River Midstream @ Bridge	Aug. 2015	-14,3	-2,26	1,9	±0.3
Swartkops River Downstream @ Bridge	Aug. 2015	-9,3	-1,3	2,6	±0.3

The results of isotopic analyses for four periods (i.e. November 2014, February 2015, June 2015 and August 2015) are tabled in Table 2. The Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL) which indicated precipitation with slopes s=8 and s=5.8, respectively, are shown in Figure 2. All other surface water sample shows the deflection from GMWL and LMWL. The residual liquid is enriched in the heavier isotope molecule because the lighter molecules move rapidly and hence has a greater tendency to escape from the liquid phase. The groundwater and spring water samples that were taken in June 2015 and including both surface and groundwater samples taken in August 2015 (Figure 2) plotted below the GMWL, however, the samples that were taken in November 2014 and February 2015 plotted above GMWL; water samples that were taken in June 2015 and August 2015 are more depleted compared to the ones that were taken in November 2014 and February 2015. This is due to temperature effect, according to Clark and Fritz, 1997 the winter rainfall has lower isotope ratios than summer rainfall. Spring, Groundwater and surface water samples collected in August 2015 indicates that the two water sources are mixing.

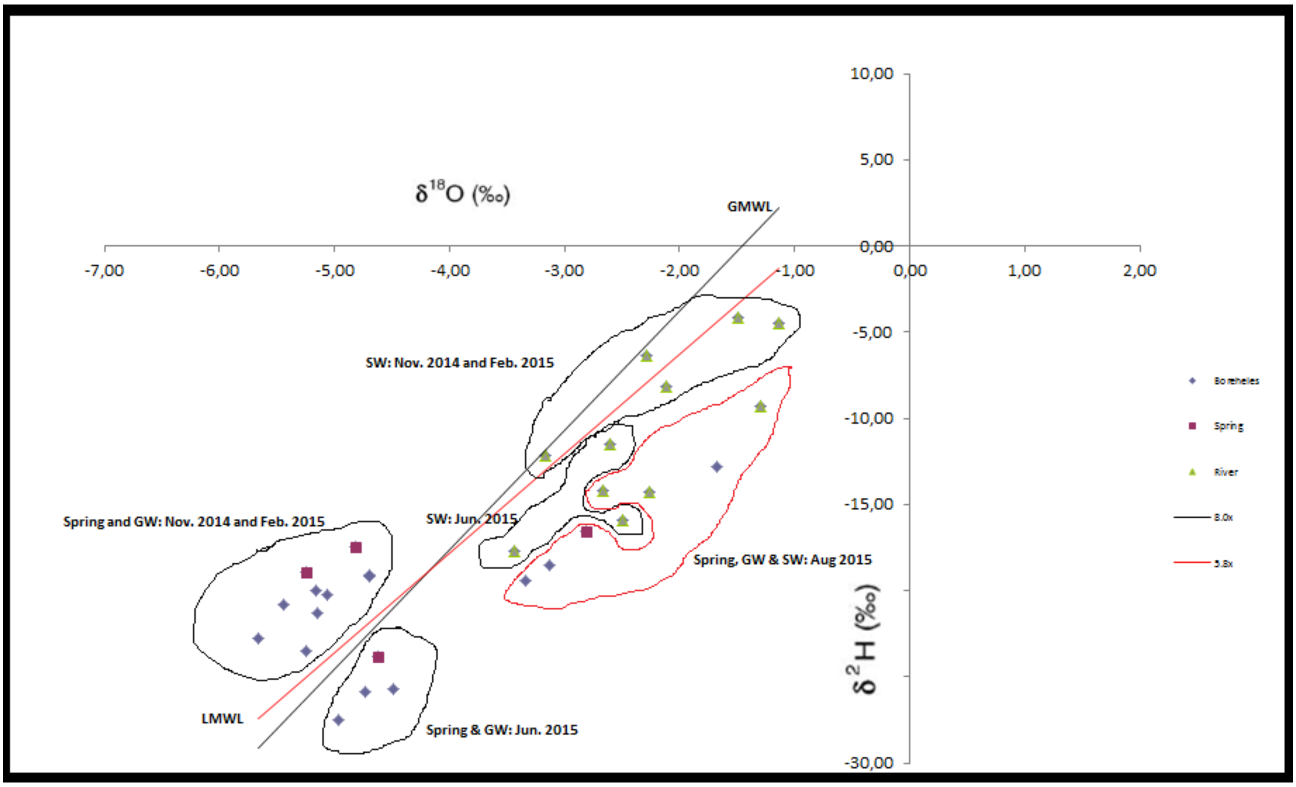

Figure 2: Show this data in a δ^{18}O vs. δ D space relative to the Global Meteoric Water Line (GMWL, Craig, 1961) and Local Meteoric Water Line (LMWL in Sandveld).

4.1.2 TRITIUM

Tritium is present in very small concentrations in the atmosphere and was used as tracer substances in this study; it was used to identify younger groundwater (water recharged after 1952). Therefore, groundwater and spring water samples, yielded water containing very low concentrations of tritium (<0.8 TU), indicating water that is more than 50 years old and this is due to radioactive decay with longer residence time in the groundwater. However, Amanzi3 yields the tritium ranges from 0.2 to 1.4, indicating young water and had chemical contents similar to the river.

4.1.3PIPER DIAGRAM

The graphs below were plotted using WISH software package and represent the groundwater chemistry data of the study area. Based on Piper diagram Figure 3 showing chemical analyses of groups of water samples from various localities in the TMG aquifer, the classification of the watertype is that dominated by Na-Cl water which is typical old marine water. However, the sample from the two boreholes Sovereign Foods at Rietheuwel and Despatch indicated Ca-Cl and Na-K water type, respectively. Sovereign Foods at Rietheuwel water sample indicates that the water is typical of mine water environment. Their electrical conductivities (EC) are 1278 and 1229.10 mS/m, respectively; they are exceeding the limit of 150 mS/m, the maximum acceptable limit for domestic use.

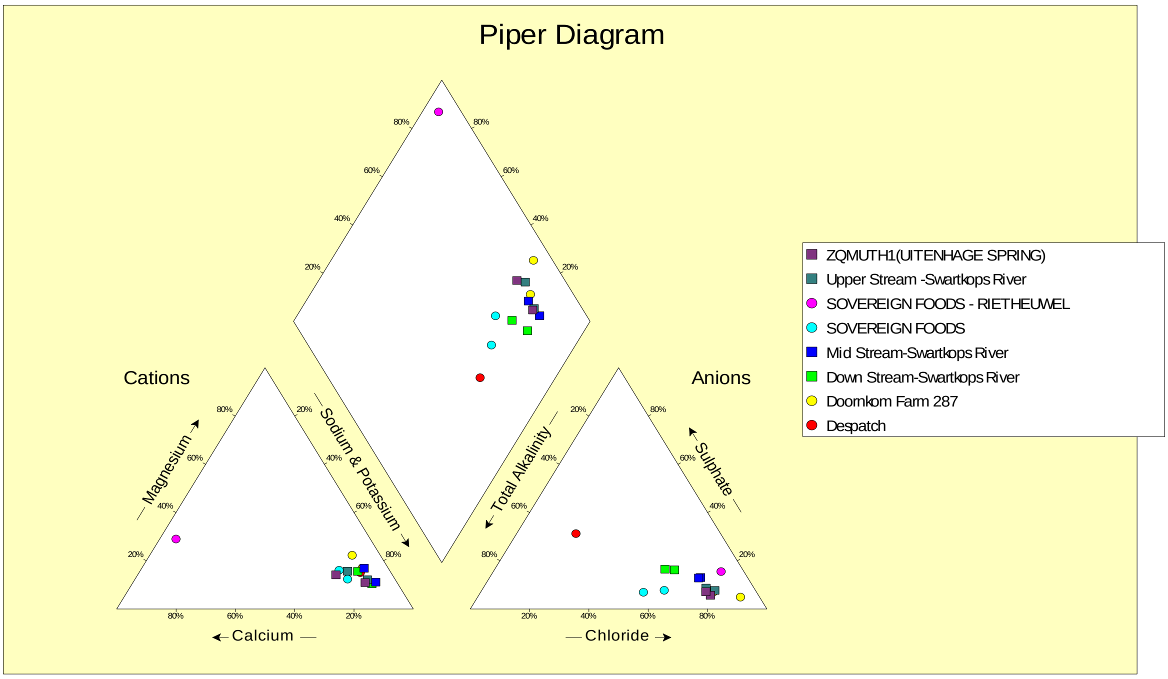

Figure 3: Piper Diagram of the Uitenhage Water Samples

Table 3: The graphs below were plotted using WISH software packaged and represent the groundwater chemistry data of the study area.

Date	Depth (m)		Sample ID	Total Dissolved Solids	Nitrate NO_3 as N	Chlorides as Cl	Total Alkalinity as $CaCO_3$	Sulphate as SO_4	Calcium as Ca	Magnesium as Mg	Sodium as Na	Potassium as K	Conductivity at 25° C in mS/m	pH-Value at 25° C	Free and Saline Ammonia as N	Fluoride as F
		Class I	(Recommended)	<1000	<10	<200	N/S	<400	<150	<70	<200	<50	<150	5-9.5	<1	<1
		Class II	(Max. Allowable)	1000-2400	10-20	200-600	N/S	400-600	150-300	70-100	200-400	50-100	150-370	4-5 or 9.5-10	1-2	1-1.5
			Duration	7 years	7 years	7 years	N/S	7 years	7 years	7 years	7 years	7 years	7 years	No Limit	None	1 year
Jun. 15	110		SOVEREIGN FOODS - RIETHEUWEL	**8562,60**	0,27	**1355,30**	184,20	355,40	**565,20**	**149,60**	16,00	**78,00**	**1278,0**	7,80	0,21	0,56
Jun. 15	152		SOVEREIGN FOODS	140,70	-0,10	37,90	26,40	6,00	5,70	3,20	22,10	7,30	21,00	6,90	-0,10	0,52
Jun. 15	n/a		ZQMUTH1(UITENHAGE SPRING)	95,14	0,14	34,60	-10,00	3,10	4,10	1,80	16,90	-1,00	14,20	5,70	-0,10	0,36
Jun. 15	100		Doornkom Farm 287	244,55	0,44	83,30	21,50	9,40	5,30	6,10	52,20	1,20	36,50	6,60	-0,10	0,53
Jun. 15	n/a		Upper Stream -Swartkops River	119,93	-0,10	41,40	-10,00	5,10	4,00	2,60	23,00	-1,00	17,90	6,90	-0,10	0,44
Jun. 15	n/a		Mid Stream-Swartkops River	**1449,21**	2,91	**469,20**	146,30	112,50	47,50	44,50	**645,00**	16,00	**216,30**	8,10	**1,68**	0,59
Jun. 15	n/a		Down Stream-Swartkops River	**1564,45**	1,50	**488,30**	258,00	170,10	53,70	38,00	**575,00**	23,30	**233,50**	8,20	**4,09**	0,74
Aug.15	**152**		SOVEREIGN FOODS	14,41	0,10	35,60	34,50	5,60	5,70	2,60	25,90	7,00	21,50	6,70	0,10	0,56
Aug.15	n/a		ZQMUTH1(UITENHAGE SPRING)	9,11	0,14	32,00	10,00	3,80	2,50	1,50	20,90	1,00	13,60	5,30	0,10	**1,10**
Aug.15	100		Doornkom Farm 287	72,90	0,55	**288,30**	28,50	19,30	18,00	25,60	152,70	1,60	108,80	**25,60**	0,10	0,34

Date	Depth (m)	Sample ID		Total Dissolved Solids	Nitrate NO3 as N	Chlorides as Cl	Total Alkalinity as CaCO3	Sulphate as SO4	Calcium as Ca	Magnesium as Mg	Sodium as Na	Potassium as K	Conductivity at 25° C in mS/m	pH-Value at 25° C	Free and Saline Ammonia as N	Fluoride as F
		Class I	(Recommended)	<1000	<10	<200	N/S	<400	<150	<70	<200	<50	<150	5-9.5	<1	<1
		Class II	(Max. Allowable)	1000-2400	10-20	200-600	N/S	400-600	150-300	70-100	200-400	50-100	150-370	4-5 or 9.5-10	1-2	1-1.5
			Duration	7 years	7 years	7 years	N/S	7 years	7 years	7 years	7 years	7 years	7 years	No Limit	None	1 year
Aug.15	n/a	Upper Stream -Swartkops River		10,18	0,10	33,40	10,00	4,90	2,50	1,90	24,00	1,00	15,20	6,60	0,10	0,10
Aug.15	n/a	Mid-Stream-Swartkops River		39,46	0,51	127,10	41,60	30,00	8,40	10,50	89,40	4,30	58,90	7,40	0,13	0,10
Aug.15	n/a	Down Stream-Swartkops River		183,65	1,98	**483,00**	306,50	181,40	55,00	46,80	**420,20**	26,90	**274,10**	8,10	**3,44**	0,38
Aug.15		Despatch		823,50	**14,57**	96,30	440,10	267,30	96,30	**84,20**	**809,90**	22,30	**1229,10**	7,80	0,10	**1,04**

4.1.4 BIOLOGICAL ANALYSES

Table 4: Bacteria Analyses

No.	Date	Site	E.Coli/100ml	Enterobacter Aerogen/100ml	Date	E. coli	Enterobacter Aerogen/100ml	P.Mirabilis/100ml	Date	E. Coli	Enterobacter Aerogen/100ml	P.Mirabilis/100ml
Surface water samples												
1.	Nov. 2014	Swartkops River Up-Stream	56	53	Jun. 215	19	9	0	Aug. 2015	0	0	7
2.	Nov. 2014	Swartkops River Mid-Stream	190	0	Jun. 215	12	1	41	Aug. 2015	5	26	44
3.	Nov. 2014	Swartkops Down-Stream	97	0	Jun. 215	7	74	39	Aug. 2015	0	0	0
Groundwater Samples												
4.	Nov. 2014	Soverign foods at Riethewel	219	51	Jun. 215	1	18	24	-	-	-	-
5.	Nov. 2014	Sovereign foods	5	32	Jun. 215	0	0	70	Aug. 2015	0	0	12
6.	Nov. 2014	Doorenkom Farm 287	166	92	Jun. 215	0	1	1	Aug. 2015	0	0	0
7.	Nov. 2014	Amanzi 3	150	0	Jun. 215	-	-	-	-	-	-	-
8.	Nov. 2014	Uitenhage Spring	7	0	Jun. 215	0	1	9	Aug. 2015	0	0	0
9.	-	Despatch	-	-	-	-	-	-	Aug. 2015	3	13	8

During wet season, the bacterial count downstream of the Swartkops River is high as compared to upstream, however there is very high count in the midstream and that may be due to lots of factors such as sewage effluents from treatment works. However, the bacterial count is vice versa during dry season. The count found in the midstream is unacceptable for freshwater, and is its occurrence in the river water can pose a treat for agricultural use.

The bacterial count in borehole samples from Doornkorn farm, Soveregn foods at Rietheuwel and Amanzi 3 was found to be high as compared to Sovereign foods. However there is abnormal count in E-Coli count in Soveriegn foods at Rieteuwel and this may be because of farming activities in this area. The bacterial count was high in ground water as compared to surface water.

E-aerogenes is a gram negative bacterium, it can be found in marine and freshwater, sewage and soils. It can cause infections such as respiratory and urinary tract infections. It is usually present in many healthy vertebrates. However it causes infections in earthworms.

The E-Aerogens in Swartkops River was high upstream as compared to downstream and this is unusual case with as it is normally known with other bacteria like E-Coli is always high downstream as compared to upstream as is known to be influenced by land based activities such as sewage works. However in the case of E-aerogens the case is different as it this study revealed that the E-aerogens count was high upstream (53.0) and low downstream (0.0). This could be due to dilution when bacteria enter the river and mix with a high volume of freshwater. In the midstream there were also low counts (0.0) as the downstream, and this may be because of the different soil structure found in this river as it is known that this bacterium is also found in the soil. This is an indication that there is a problem of water quality downstream as the E-aerogens start to be depleted, this may be due to waste water discharge in the midstream going to downstream.

There has been a different case with regard to the presence of this bacterium in groundwater as the data indicate that there was high count of E-aerogen in Sovereign foods and Doornkom farm boreholes. These sites indicated high count of E-aerogen, and this gives a conclusion that for this study it was found that E-aerogen was high in groundwater as compared to surface water (Table 5).

5. CONCLUSION

From the observations in Figure 2 above, there is no interaction between surface water and groundwater. Therefore we conclude that water from the spring is derived from the old groundwater. This indicates that the aquifer system is not in hydraulic connection with the river. However, Amanzi 3 is an artesian borehole which indicated the mixing of sub-modern and modern water. From Table 2 above it was noticed that the tritium values for Doornkom in February 2015 and June 2015 are indicating the recent recharge from the rainwater. It was also noted that the tritium values in June 2015 for both groundwater and surface water were increased; and this is due to the winter rainfall recharge.

The chemical analysis (Figure 3) results of groups of water samples from various localities in the TMG aquifer, the classification of the water type is that dominated by Na-Cl water which is typical old marine water. However, the sample from Sovereign Foods at Rietheuwel indicated Ca-Cl water type, typical of mine water environment. Its electrical conductivity (EC) is 1278 mS/m exceeding the limit of 150 mS/m, the maximum acceptable limit for domestic use. This could be due to the farming activities from the chicken farm. Swartkops River is an ephemeral, therefore it is expected that diffuse recharge occurs into the shallow aquifer.

During wet season, the bacterial count downstream of the Swartkops River is high as compared to upstream, however there is very high count in the midstream and that may be due to lots of factors such as sewage effluents from treatment works. However, the bacterial count is vice versa during dry season. This could be due to dilution when bacteria enter the river and mix with a high volume of freshwater or the sewage systems management and treatment has been improved.

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