THE CHEMICAL GROUNDWATER CHARACTERISTICS OF THE SUTHERLAND AREA, NORTHERN CAPE.

By

SHAFICK ADAMS

Submitted for the fulfillment
of the requirements for the degree

MAGISTER SCIENTIAE

in the Faculty of Science,
School of Environmental Studies,
Earth Sciences Department,
University of the Western Cape.

Supervisors: R. Titus
Dr G. Tredoux

November 1998

DECLARATION

I declare that The Chemical Groundwater Characteristics of the Sutherland Area, Northern Cape is my own work and that all the sources I have used or quoted, have been indicated and acknowledged by means of complete references.

ETHICAL CONSIDERATION

The results of this study would be made available to the Sutherland municipality and farmers of the region. All the farmers who allowed me access to their boreholes can utilise the results and data contained in this thesis. The author hopes that the results of this study be used to develop and manage the groundwater resources more effectively for generations to come.

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Shafick Adams
November 1998

ACKNOWLEDGEMENTS

This project was made possible through the funding of the Water Research Commission of South Africa.

I thank Rian Titus, Kevin Pietersen and Dr Gideon Tredoux for their comments and advice during the project and for their invaluable input during the drafting stages of this project.

Informative discussions with Allan Woodford and Dr Luc Chevallier from the Department of Water Affairs and Forestry and the Council for Geoscience respectively, in the initial stages of the project, are acknowledged.

I am indebted to Ari van Deventer (Infruitec), Mike Louw from the Council for Scientific and Industrial Research (CSIR), Andrew Pascal (CSIR) and Dr Chris Harris (Stable Isotope Laboratory, University of Cape Town) who conducted the chemical and isotopic analyses. Without good quality data, one cannot do a good quality project.

I would like to thank Clive Paulse, University of the Western Cape (UWC), for the preparation of the hydrochemical contour maps.

Thank you to Rudi Blom (Cottage Guest House, Sutherland) for making my days pleasurable during the fieldwork stage of this project.

Thanks to all the farmers who allowed me to visit their boreholes and for their interesting discussions.

Thanks to Brian Lawrence (UWC) for the logistical support given during this project.

This work would not have been possible without the continuous support, patience and encouragement of my family, friends and friend for life, Mary-Rose.

I dedicate this work to all my family and friends.

ABSTRACT

The objectives of the project were to establish, identify, interpret and map the chemical groundwater composition of the area surrounding the town of Sutherland. Processes that govern the groundwater chemistry of the area are identified and interpreted.

The study area is underlain by the fractured rocks of the Abrahamskraal formation of the Beaufort Sequence, Jurassic dolerites and intrusives associated with the Salpeterkop Carbonatite Complex. The groundwaters naturally evolve from a Ca-HCO_3 to a Na-Cl type water with Na-HCO_3, Ca-SO_4, Na-SO_4 and Ca-Cl being the intermediate water types formed. Statistical, graphical and hydrochemical techniques are used to characterise the groundwater composition of the fractured aquifers in the Sutherland region.

The statistical techniques, specifically descriptive, Pearson's correlation matrices and varimax rotated factor analyses were used on the hydrochemical data set. The statistical analyses aided in reducing the rather large data set to the more significant variables that impact on the groundwater composition. The results of the statistical analyses coupled with graphical methods and the stable isotopes (^{18}O and ^{2}H) suggested that topography, evapotranspiration, geology and anthropogenic influences are the major factors responsible for the groundwater composition of the area. A number of processes were identified that occur within the subsurface.

Rainwater charged with biogenic CO_2, infiltrates into the subsurface where it dissolves carbonate-containing minerals, mostly $CaCO_3$. In flatter areas, where infiltration is slow, the infiltrating water leaches evaporitic salts to the subsurface. Thus, in higher lying areas where salt leaching is absent, Ca-HCO_3 type waters would form. Where salt leaching is predominant, Na-Cl type water may form. Na-Cl type waters also form because of natural hydrogeochemical evolution. Through the mechanism of cation exchange Na-HCO_3 waters are formed where Ca is exchanged mainly by bound Na. Precipitation of calcite out of a solution results in the dissolution of gypsum

($CaSO_4.2H_2O$), fluorite (CaF_2) and carbonate minerals (i.e. strontianite). Formation of Ca-SO_4 waters is formed in this manner. Exchangeable Na is released and Ca is taken up by the geological matrix forming a Na-SO_4 type water. At higher salinities, the process of reverse cation exchange results in the Ca-Cl type water from Na-Cl water, whereby Na is replaced by bound Ca. The presence of Ca-Cl type water is indicative of mixing or dilution of a more saline and older water by a fresher, younger water dominated by Ca ions. Elements that do not contribute significantly to the groundwater salinity such as Mg, K, Sr and Ba participate in cation exchange processes but are masked by the major ions Ca, Na, Cl, HCO_3 and SO_4.

The processes of dissolution, precipitation and cation exchange coupled with the physical environment, result in the hydrogeochemical groundwater evolution of the area. Superimposed on the processes occurring in the subsurface are the effects of concentration by means of evapotranspiration and land use practices. Irrigation return flows together with the high evaporation rates increases the formation of the already high natural soluble salts in the unsaturated zone. Nitrate pollution from animal wastes causes isolated instances of pollution of the fractured rock aquifers.

In order to supply potable groundwater to the area it is recommended that boreholes, if possible, be situated away from topographical flat areas. Monitoring programs should also be initiated to determine the changes of the groundwater over time.

ABBREVIATIONS

AEC - Atomic Energy Corporation
DWAF - Department of Water Affairs and Forestry
GMWL - Global Meteoric Water Line
pers. comm. - personal communication

Name	Abbreviation	Unit
Correlation coefficient	r	
Deuterium	^2H or D	per mil
Electrical conductivity	EC	mS/m
Metres	m	m
Milligrams per litre	mg/l	mg/l
Oxygen-18	^{18}O	per mil
Partial pressure of *carbon dioxide*	pCO_2	atm
Parts per million	ppm	ppm
Redox potential	Eh	mV
Saturation index	SI	
Total dissolved solids	TDS	ppm or mg/l

CATIONS	Aluminium	Al^{3+}	CATIONS	Strontium	Sr^{2+}
	Barium	Ba^{2+}		Uranium	U^{6+}
	Boron	B^{3+}		Zinc	Zn^{2+}
	Calcium	Ca^{2+}		Hydrogen	H^+
	Copper	Cu^{2+}	ANIONS	Bicarbonate	HCO_3^-
	Iron	Fe^{2+}/Fe^{3+}		Carbonate	CO_3^{2-}
	Magnesium	Mg^{2+}		Chloride	Cl^-
	Manganese	Mn^{2+}		Fluoride	F^-
	Nickel	Ni^{2+}		Nitrate	NO_3^-
	Potassium	K^+		Phosphorus	P^{3-}
	Sodium	Na^+		Sulphate	SO_4^{2-}

TABLE OF CONTENTS

CHAPTER 1
GENERAL INTRODUCTION

CHAPTER 2
THEORETICAL CONSIDERATIONS

CHAPTER 3
STUDY AREA

CHAPTER 4
METHODOLOGY AND CONCEPTUAL MODELS

CHAPTER 5
HYDROGEOCHEMISTRY

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

LIST OF APPENDICES

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Groundwater, an important natural resource, in the Sutherland area is highly variable in its chemical character. The region depends entirely on groundwater for domestic and agricultural usage as no adequate surface waters or piped water exists. The variability in the quality of the groundwater is the result of the various processes and activities occurring at the surface and the subsurface.

The groundwater mainly occurs in fractured aquifers and is exploited by means of boreholes. Siting of these boreholes is too often based on unscientific procedures, resulting in boreholes with various yields and qualities. An understanding of the region's hydrogeological/geomorphological conditions, which in turn influences the chemical quality of the water, is thus important to understand the groundwater characteristics of the area. The chemical composition of the groundwater can be used to describe the interaction of the subsurface water with its environment.

It is postulated that groundwater chemistry can elucidate the characteristics of the aquifers found in the study area, the factors and processes that determine its constituents and how these differ in space and time. Thus, by deciphering the main factors and processes that determine the variability in the groundwater chemistry, areas can be delineated that is favourable or unfavourable for the occurrence of groundwater of a suitable quality for domestic and agricultural usage.

1.2 BACKGROUND TO THE STUDY

This study forms part of a five-year project entitled: "A groundwater supply assessment and strategy for the Western Karoo, Namaqualand and Bushmanland". The Water Research Commission funds this project.

Groundwater is gaining increasing importance in the supply of water to rural communities in the drier regions of South Africa where surface waters are very scarce or absent. Assessing the groundwater characteristics was thus important, mainly in terms of quality. Assessing the quantity that the aquifers yield falls beyond the scope of this project.

Understanding the area's potable groundwater resources is important, as it is the only source of water for the local communities and farmers. As the importation of surface water over very long distances is very costly.

No serious attempt has previously been made to assess the water quality, and thus the groundwater chemistry of the area. Management and monitoring systems are absent. The need for adequate groundwater management and monitoring is increasing and can only be achieved if enough data are available on the existing water resources like boreholes and wells. Two sets of data are required to formulate these management strategies, namely quantity and quality data.

This study focuses mainly on the groundwater chemistry/quality, to evaluate and define the aquifers of the Sutherland area. However, this study will try to prevent a data-rich and information-poor situation, by analysing and interpreting the data and try to correlate the results obtained with the physical and human environment.

1.3 OBJECTIVES OF THE STUDY

The objectives of the study were to:

(1) Establish the chemical composition of groundwater.

(2) Identify and interpret the different water qualities.

(3) Map the groundwater in terms of distribution and chemistry in the areas surrounding Sutherland.

(4) Identify the hydrogeologic and geomorphological conditions that influence the chemical composition of the groundwater.

1.4 RESEARCH REQUIREMENTS

To achieve the above objectives, the following research requirements were identified:

(1) Sampling of individual boreholes for chemical and isotopic analyses (for selected boreholes) and recording its physical parameters (e.g. pH, alkalinity, temperature, geological and geomorphological setting and depth to water).

(2) Developing conceptual models for a fractured rock aquifer.

1.5 ORGANISATION OF THE STUDY

The first four chapters mainly concentrate on the descriptive and observational characteristics of the area. The remaining chapters focus on the presentation and interpretation of the chemical data.

Theoretical considerations are reviewed in Chapter 2.

Chapter 3 describes the study area.

Methodologies and presentation of conceptual models are outlined in Chapter 4.

The geohydrochemistry is discussed in Chapter 5 in terms of the hydrogeochemical processes, its distribution and its relation to the physical environment.

Conclusions and recommendations are made in Chapter 6.

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 INTRODUCTION

Existing literature, comprising of both local and international literature, is reviewed in this chapter. Literature surveyed and reviewed was of areas experiencing similar or nearly similar conditions to that found in the specific study area (i.e. arid to semi-arid climate and similar geological conditions). The literature study significantly contributed to the formulation of the conceptual models outlined in Chapter 4. Relevant literature will also be incorporated in subsequent chapters to aid interpretation.

2.2 PREVIOUS WORK

No previous water quality studies have been done or published for the study area. One report on the geohydrology of the Sutherland area could be found (DWAF, 1946). This two-page report only dealt with the siting of a few boreholes on the farm Kruisrivier. The Department of Water Affairs and Forestry (DWAF) did several geohydrological surveys around Williston (Seward, 1983, 1986). Hydrogeological investigations in the vicinity of Merweville (Diettrich, 1973) and Fraserburg (Wilke, 1962) provided the only real information found for the Western Karoo in the immediate vicinity of the study area. To date most of the geological work done in the area was centred on Salpeterkop, a carbonatite extrusive structure (De Wet, 1975; Newton, 1987; Verwoerd, 1990; Verwoerd et al., 1995).

The Geological Survey of South Africa mapped the structures (dykes, major joints and fractures) in the study area (Chevallier, pers. comm.). The Geological Survey has interpreted the geology of the area on 1:250 000 (Theron, 1983) and 1:50 000 scale geological maps, the latter unpublished.

2.3 LITERATURE REVIEW

2.3.1 Fractured rock aquifers/formations

It is well recognised that the quality of groundwater varies considerably over short distances in many of South Africa's fractured aquifers (Parsons and Tredoux, 1993). More than 90% of the aquifers in South Africa are fractured aquifers (Kirchner and Van Tonder, 1995). Except for some localised occurrences of permeable porous Cretaceous and Karoo sandstones, pre-Tertiary formations do not feature as primary aquifers (Vegter, 1995) in the study area.

Kirchner and Van Tonder (1995) defined the term fracture as cracks, fissures, joints and faults, which are caused mainly by:

(1) Tectonic movement, secondary stresses, release fractures, shrinkage cracks, weathering, chemical action and thermal action.

(2) Petrological factors like the compositions of minerals, internal pressures and grain sizes.

A fractured rock mass can be considered a multi-porous medium, consisting of two main components, namely matrix rock blocks and fractures (Kirchner and Van Tonder, 1995). Fractures are conductivity conduits for flow whilst the matrix blocks may be permeable or impermeable, with most of the storage contained within the permeable matrices (Kirchner and Van Tonder, 1995). The density of fractures may also be a factor in storing significant amounts of water and depends on the lithology and structural components of the geological setting. Thinner sedimentary rocks can be more susceptible to fracturing than thicker sedimentary rocks units (Domenico and Schwartz, 1990). Hughes and Sami (1991) found that the sandstones of the Bedford catchment have undergone a high degree of lithification and assumed that they deform in a brittle fashion and fracture in response to stresses. The mudstones behave in a more ductile fashion (due to their high clay content) within this catchment. Fractures may close at depth, due to the weight of the overlying material. The openings develop typically in the upper part of the earth's crust, being generally restricted to the upper 100 m (Wright, 1994).

Dolerite intrusions are common in Karoo aquifers and experience has proven that their location is often associated with high yielding boreholes due to the fracturing they have caused in the adjacent country rocks (Enslin, 1950). Jointing is common along these intrusive contacts and they are particularly valuable on the upslope side of the hydraulic gradient in the Karoo sediment (Robins, 1980). Major joint directions in the Karoo sediments near Sutherland are north and east-north-east (Theron, 1983). Karoo sediments have a poor primary permeability but the intrusive contacts form high-permeability conduits that can draw from a wide area of the sediments and support sustained yields of up to 6 l/s, as found by Robins (1980) in Swaziland. Increased yields could also be associated with fracturing and other deformational features such as fold axes and faults. Weaver et al. (1993) found in the Strydenberg region that not all dolerite contacts yield water.

2.3.2 Recharge

It could be stated that the groundwater quality (salinity) depends on the amount of rainfall infiltration that contributes to recharge (AEC, 1990). There is a general correlation between mean annual rainfall and groundwater quality with poorer quality water being associated with areas receiving a low average rainfall. It is noticeable that areas receiving less than 2250 mm/annum tend to exhibit the poorest water quality (AEC, 1990). De Beer and Blume (1985) suggest that the water in the Karoo sequence is generally of a poor quality. The higher the rainfall the better the quality of groundwater, although superimposed on this is more local specific factors depicting the quality of groundwater (AEC, 1990).

The water bearing formations of South Africa are recharged by rain infiltration, which can amount to 3% of mean annual recharge in the west, with an average annual rainfall of 250 mm, to 23% in the east, with an average rainfall of 1200 mm (Simonis and Kok, 1989). The secondary Karoo aquifers have limited storage (S) (S = 0.004) and recharge rates of between 2-5 % of annual precipitation (Bredenkamp et al., 1995; Van Tonder and Kirchner, 1990). Annual recharge may also be erratic because of the variability of rainfall. The amount of recharge depends on the head differential and the hydraulic properties of the aquifers. Recharge from natural sources includes the following (US Dept. of the Interior, 1981):

(1) Deep percolation of precipitation as a major source of groundwater recharge.

(2) Seepage from surface water bodies is another important source of recharge. In arid regions where the entire flow of streams may be lost to an aquifer, seepage may be of major significance.

(3) Recharge by means of underflow from a nearby, hydraulically connected aquifer.

The amount of recharge is influenced by vegetative cover, topography and nature of soils and the type, intensity and frequency of precipitation (US Dept. of the Interior, 1981). Groundwater levels tend to rise during rainy periods or after a heavy storm. This is due to the fact that the joints penetrated by the boreholes are in hydraulic continuity with the joints that are open to recharge (Robins, 1980). The favoured recharge mechanism in Karoo aquifers is flow along preferred pathways (Van Tonder and Kirchner, 1990). In general, shallow water levels occur in areas of outcrop and recharge, whereas deep water levels coincide with basement depressions having thickened beds and a lack of recharge (Levin, 1981). Groundwater generally moves from levels of higher potential energy to levels of lower potential energy. The energy is essentially the result of elevation and pressure (Davis and De Wiest, 1966).

2.3.3 Natural hydrogeochemistry

Katz and Choquette (1991) state that the chemical composition of groundwater that is unaffected by human activities, is determined by a series of complex physical, chemical and biological processes occurring as the water derived from precipitation moves through soil, the unsaturated zone and the saturated zone. The hydrogeochemistry of groundwater reflects the source of the water, the lithology of the aquifer and the local chemical conditions such as temperature, pressure and redox potential (Henderson, 1986). Hydrochemical analysis of groundwater is thus not only useful for determining the potability of groundwater, but also in understanding the geology and movement of groundwater (Ophori and Toth, 1988). The chemical constituents of groundwater commonly reflect the environment of occurrence including, geological, biospherical and human influence (Malomo et al., 1990). According to Tredoux and Kirchner (1981), an intimate knowledge of the chemical evolution of the water in an aquifer is required in order to classify the water sources and to identify the groundwater mixture.

Water naturally contains a number of different inorganic constituents. The major cations are calcium, magnesium, sodium and potassium, the major anions are chloride, sulphate, carbonate and bicarbonate. Although not in ionic form, silica can also be a major constituent. In addition, there may be minor constituents present such as iron, manganese, fluoride, nitrate, strontium and boron (Fetter, 1988).

2.3.3.1 Weathering and dissolution

The weathering of rocks is both a chemical and mechanical process (Henderson, 1986). The weathering process entails the interaction of an aqueous solution with rock material to produce a solution of different composition from the reactant one, a residue of insoluble solids of the initial rock and other solids that are secondary mineral phases (Henderson, 1986). On encountering soil and rock, water incorporates major and trace elements by decomposing and dissolving rock minerals. For the most part this is accomplished by reaction of the H^+ ion with carbonate and alumino silicate minerals to liberate cations and silica into solution and leave behind clay minerals (Rose et al., 1979). Chemical weathering is thus an important process that can neutralise incoming acidity. Weathering of minerals generally exhibits two types of reactions (Henderson, 1986):

(1) Congruently whereby all minerals dissolve completely.

Example:

$$\underset{\text{Quartz}}{SiO_2} + 2H_2O \rightarrow \underset{\text{Silicic acid}}{H_4SiO_4}$$

(2) Incongruently whereby some minerals dissolve and others recombine to form a new solid phase.

Example:

$$\underset{\text{Magnesite}}{MgCO_3} + 2H_2O \rightarrow \underset{\text{Brucite}}{Mg\,(OH)_2} + HCO^-_3 + H^+$$

The amount of carbonates, bicarbonates and dissolved carbon dioxide (CO_2) largely controls the pH of water (El Ghandour et al., 1985). The type of contamination bases, degree of ionisation, extent of hydrolysis and buffering actions governs the pH of water (El Ghandour et al., 1985). Strong acids from precipitation, together with carbonic acid from biological processes in the soil, attack minerals and release dissolved components to the water (Katz and Choquette, 1991). If the aggressive weathering agent is a strong acid from precipitation, the accompanying anion (SO_4^{2-}, NO_3^- or Cl^-) will balance the base cation released (Katz and Choquette, 1991). If carbonic acid is the principal weathering agent the bicarbonate anion will balance the cations released (Katz and Choquette, 1991).

The carbonate ions are mainly derived from calcium carbonate rocks, which generally have low solubilities, however, in the presence of dissolved CO_2 the rocks become highly soluble forming bicarbonates (El Ghandour et al., 1985). This suggests that the content of bicarbonate in solution is dependent on the amount of CO_2 in water. Carbon dioxide can be present in soil gas and will react with precipitation percolating through the unsaturated zone, or can be due to methanogenesis and possibly other bacterially mediated processes in groundwater (Katz and Choquette, 1991). The initial source of dissolved CO_2 is rain, which leads to the dissolution of $CaCO_3$ to its equivalent calcium and bicarbonate ions. The biological activity in the soil and the chemical processes release considerable amounts of CO_2, which help in the contamination of groundwater with bicarbonate ions (El Ghandour et al., 1985).

The chemical characteristics of water at depth would thus differ from those that are found in shallow depths. The effect of temperature and pressure on mineral solubilities and ion complexing and the great ages of deep groundwater are factors that produce different water compositions (Freeze and Cherry, 1979).

Groundwater chemistry is dominated by the faster reacting minerals [muscovite, andesine (feldspar), calcite and chlorite] while the influence of slow reacting minerals such as quartz is negligible (Katz and Choquette, 1991). Water charged with carbon dioxide reacts with feldspars and depending on the type of feldspars, waters with predominantly dissolved sodium, calcium or potassium bicarbonates are formed (Mazor et al., 1980). Carbonates, chlorides, calcium, magnesium and sulphates are the major ions contributed to waters in areas of Palaeozoic and Mesozoic sedimentary rocks (DWAF, 1993).

2.3.3.2 Cation exchange

Numerous minerals exhibit the property of exchanging cations within their structure and with cations in the surrounding water (Talma, 1981). The degree of ionic exchange is dependent on such factors as charge, ionic radius and valency of the participating ions (Cogho et al., 1992). A further process of ionic exchange occurs later in the sedimentary cycle where the clay minerals adjust geochemically to the depositional environment by exchanging some of its 'detrital' elements with those present in the surrounding aqueous environment (Zawada, 1988). The usual exchange combination is the replacement of Na in a Cl dominated water by an equivalent amount of Ca derived from the aquifer rock. The cation exchange process may be exemplified by (Appelo and Postma, 1994):

$$Na^{+} + ½Ca\text{-}X \leftrightarrow Na\text{-}X + ½Ca^{2+}$$

The process of reverse ion exchange or refreshening may be represented by (Appelo and Postma, 1994):

$$½Ca^{2+} + Na\text{-}X \leftrightarrow ½Ca\text{-}X + Na^{+}$$

where: X = soil exchangers

If refreshing occurs then Na replaces Ca in solution by the action of reverse cation exchange. The most important cation exchange reactions in groundwater systems are between the following divalent and monovalent cations (Freeze and Cherry, 1979):

$$Na^{+} - Ca^{2+} ; Na^{+} - Mg^{2+} ; K^{+} - Ca^{2+} \text{ and } K^{+} - Mg^{2+}.$$

Ion replacement thus follows the sequence monovalent < divalent < trivalent and it becomes more difficult to remove the ion from a clay mineral and the affinity for adsorption is greater (Cogho et al., 1992).

2.3.3.3 Precipitation and saturation states

The dissolution of minerals because of weathering and the subsequent exchange between cations leads to the precipitation of minerals. Precipitation only occurs once the equilibrium state of mineral phases has been surpassed. Precipitation (i.e. rain and snow) and groundwater, as the two end members of a sequence, can be compared using mass-balance calculations to evaluate the relative importance of weathering (mineral dissolution) and precipitation reactions in controlling the chemical composition of groundwater (Katz and Choquette, 1991).

Saturation indices (SI) are indicative of the saturation state of a specific water with respect to specific mineral phases. Saturation indices were calculated with the NETPATH computer program, through a WATEQF subroutine (Plummer et al., 1992). The SI is expressed as (Appelo and Postma, 1994):

Degree of saturation = log IAP/KT

where: IAP = ion activity product
KT = solubility product

if: SI = -0.1 to 0.1 (saturated)
SI = -1.0 to -0.1 (undersaturated)
SI = 0.1 to 1.0 (oversaturated)

Equilibrium states are not common in groundwater (i.e. SI = 0) and the saturation states of the groundwater merely indicate the direction in which a process may proceed if it occurs at all (Appelo and Postma, 1994). Oversaturation suggests that the precipitation of minerals can occur and undersaturation suggests that the dissolution of minerals will occur if they are present. The reason for not taking SI = 0 as equilibrium in this study is due to the uncertainties in measured pH values. An error of ±0.05 pH units leads to an uncertainty of ±0.05 units in SI of minerals and in view of uncertainties in Ca^{+}, Mg^{2+} and HCO_3^- analyses. The total uncertainties are in the order of ±0.1 units of SI (Langmuir, 1971).

2.3.3.4 Elemental sources

The origin of various dissolved constituents in water (or the lack thereof) may be the result of the above processes.

Most **carbonate and bicarbonate ions** in groundwater are derived from CO_2 in the atmosphere, CO_2 in soil and the solution of carbonate rocks (Davis and De Wiest, 1966). The atmospheric CO_2 content of 0.03 percent is increased up to one hundred fold in the soil atmosphere due to root respiration and the decay of soil organic matter.

A solution of this CO_2 in water dissolves carbonate minerals (Talma, 1981) by the reaction:

$$CO_2 + (Ca, Mg)CO_3 + H_2O \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$
$$\text{and } HCO_3^- \rightarrow CO_3^{2-} + H^+$$

Other potential reactions forming bicarbonate in groundwater are the weathering of silicate rocks or the oxidation of sedimentary organic material (Talma, 1981). Sodium bicarbonate and carbonate are highly soluble and remains in the water while calcium carbonate is removed by ion exchange and replaced by sodium. It is thus suggested that waters, which are dominated by sodium bicarbonate, are formed in this way (Mazor et al., 1980).

Subsurface waters in contact with sedimentary rocks of marine origin, derive most of their **calcium** from the solution of calcite, aragonite, dolomite, anhydrite, fluorite and gypsum (Davis and De Wiest, 1966; Hem, 1989). In igneous and metamorphic rocks, weathering also release calcium from such minerals as apatite, wollastonite, fluorite and various members of the feldspar, amphibolite and pyroxene groups (Davis and De Wiest, 1966). Calcium carbonates are easily soluble in water provided there is an abundant supply of H^+ (Davis and De Wiest, 1966). The dissociation of carbonic acid is one of the most important sources of hydrogen ions (Davis and De Wiest, 1966).

The most common sources of **magnesium** in the hydrosphere are dolomite in sedimentary rocks, olivine, biotite, hornblende, magnesite and augite in igneous rocks, and serpentine, talc, diopside and tremolite in metamorphic rocks (Davis and De Wiest, 1966; Hem, 1989). In addition, most calcite contains some magnesium. A solution of limestone commonly yields abundant magnesium as well as calcium (Davis and De Wiest, 1966). Pyroxenes and olivines on reaction with CO_2-containing water are a major source of magnesium in water (Mazor et al., 1980).

The primary source of most **sodium** in natural water is from the release of soluble products during the weathering of plagioclase feldspars (Davis and De Wiest, 1966). All natural waters contain measurable amounts of sodium. Actual concentrations range from about 0.2 ppm in rain and snow to more than 100 000 ppm in brines in contact with salt beds (Davis and De Wiest, 1966). In areas of evaporite deposits, the solution of halite is important. Clay minerals may, under certain conditions, release large quantities of exchangeable sodium. Less important sources of sodium in natural water are the minerals nepheline, sodalite, stilbite, natrolite, jadeite, arfvedsonite, glaucophane and aegerite (Davis and De Wiest, 1966). These minerals are locally abundant in some igneous and metamorphic rocks, but are quantitatively of minor importance in comparison with the feldspars (Davis and De Wiest, 1966). Irrigation runoff commonly leaves a sodium residual that is much higher in concentration than the original irrigation water (Hem, 1989).

Common sources of **potassium** are the products formed by the weathering of orthoclase, microcline, biotite, leucite and nepheline in igneous and metamorphic rocks (Davis and De Wiest, 1966).

Iron is released naturally into the aquatic environment from the weathering and leaching of sulphide ores (pyrite, FeS_2) in igneous, sedimentary and metamorphic rocks. However, iron is only released under reducing conditions (DWAF, 1993). Ferrous iron (Fe^{2+}) is the most common iron species found in groundwater (Hem, 1989). Some of the important minerals and mineral groups that may contain large amounts of iron are pyroxenes, amphiboles, magnetite, pyrite, biotite, olivine and garnets (DWAF, 1993; Hem, 1989). The weathering of these minerals releases large quantities of iron which are usually converted to the relatively insoluble and stable iron oxides (Davis and De Wiest, 1966). When groundwater containing ferrous iron is exposed to the atmosphere, the following reaction occur (Davis and De Wiest, 1966):

$$2Fe^{2+} + 4HCO_3^- + H_2O + 0.5O_2 \rightarrow 2Fe(OH)_3 + 4CO_2$$

Although the removal of OH^- ions in this reaction tends to lower the pH, the solubility of ferric hydroxide is so low in the normal pH range that most of the iron will be precipitated (Davis and De Wiest, 1966).

Sedimentary rocks, particularly organic shales, may also yield large amounts of **sulphates** through the oxidation of marcasite and pyrite. Sulphate-reducing bacteria derive energy from the oxidation of organic compounds and in the process obtain oxygen from the sulphate ions in subsurface water (Davis and De Wiest, 1966). The resulting reduction of sulphate ions produces hydrogen sulphide gas as a by-product. If iron is present in the water under moderately reducing conditions, iron sulphide may be precipitated, thus removing both iron and sulphide from the water. If soil bacteria accomplish the sulphate reduction, much of the hydrogen may escape directly to the atmosphere.

Fluoride in domestic water sources is a problem in certain areas of South Africa, such as the Karoo, where concentrations in surface waters and groundwater are high (DWAF, 1993). Fluoride is thought to be one of the main ions responsible for solubilising beryllium, scandium, niobium, tantalum and tin in natural waters (DWAF, 1993). The natural concentration of fluoride appears to be limited by the solubility of fluorite (CaF_2), which is about 9 ppm fluoride in pure water (Davis and De Wiest, 1966).

2.3.3.5 Salinisation of groundwaters

Salinisation of groundwater can occur during events of recharge. The salinity may be derived from incompletely leached evaporite horizons in closed surface basins such as pans and from salt loads, built up in the unsaturated zone during periods of low rainfall (Verhagen, 1985). Sami (1992) states that, as evaporation exceeds precipitation throughout most of the year, leaching is limited and soluble salts tend to accumulate near the soil surface. Runoff and percolation periodically flush these salts into streams and groundwater after large rain events. Mazor et al. (1980) found that sodium chloride (NaCl) is dissolved from rocks, mainly from Ecca shales. In arid and semi-arid regions, two factors assume importance, namely precipitation of minerals and evapotranspiration of water. Evaporation of water from the soil and transpiration by plants may concentrate the dissolved solids to a significant degree (Rose et al, 1979). If the climate is dry, the salt content is higher and mostly the salts of sodium, NaCl and Na_2SO_4 (sodium sulphate) are found (Rethati, 1983). Arid zones thus have significant water quality problems. The slow circulation of groundwater results in mineralisation. In addition, evaporation of groundwater from discharge areas results in salt deposition, with consequent high salinity in the soil and shallow groundwater (Fetter, 1988).

2.3.3.6 Hydrochemical evolution

The length of groundwater flow paths and residence times can influence the chemical composition of water in an aquifer (Katz and Choquette, 1991). Kauffman (1977) states that the progressive increase in mineralisation along the valley-wide flow path is primarily a function of the chemical quality of water in the recharge zone. The type, distribution and adsorptive capacity of the geological matrix, the porosity and permeability of the rocks and sediments and the course followed by the water along a flow path is also contributing to progressive mineralisation (Kauffman, 1977). It is postulated that the order in which groundwater encounters strata of different mineralogical composition, can exert an important control on the water chemistry (Freeze and Cherry, 1979). They also found that as groundwater flows through strata of different mineralogical compositions, the water undergoes adjustments caused by imposition of new mineralogical controlled thermodynamic constraints. Although in some strata the water may attain local equilibrium with respect to some mineral phases, the continuous flow of the water causes disequilibrium to develop as the water moves into other strata comprising of different minerals (Freeze and Cherry, 1979). A striking feature of many groundwaters in stratified sedimentary sequences, is the occurrence of Na^+ and HCO_3^- as dominant ions (Freeze and Cherry, 1979). Results of a field sampling program in Dodge and Fond du Lac counties, Wisconsin (USA), indicate that significant changes in groundwater chemistry occur across the boundary between unconfined and confined regions of the sandstone aquifer. These included an increase in sulphate, chloride, sodium and potassium concentrations and a less pronounced increase in radium activity (Weaver and Bahr, 1991). Hydrogeological contour maps where the contours cut across geological boundaries, indicate the reduced influence of geology in determining the water chemistry.

Contrasts in the chemical quality of water in the three common groups of sedimentary rocks (i.e. sandstone, shale and carbonates) are usually quite marked. Shale most commonly contains higher amounts of iron, fluoride and a low pH that are typically between 5.5 and 7.0 (Davis and De Wiest, 1966). The most abundant minerals in shales (e.g. illite and quartz) are relatively unreactive in the weathering environment and contribute relatively little to runoff chemistry. Waters draining shales also often contain chloride and sodium. These are thought to originate from seawater trapped in the shale at the time of deposition, however, the form in which these ions are stored is not known (Drever, 1988). Thus, waters draining shales are highly variable in composition. They usually have sulphate or chloride as major anions and lower silica to total cation ratios than waters draining igneous rocks. Limestone will have a lower silica (SiO_2) content and a greater amount of calcium and magnesium with pH values generally above 7.0 (Drever, 1988). Limestones weather more rapidly than igneous rocks. As a result, water draining limestones are more concentrated than those draining igneous rocks (Drever, 1988). The quality of water draining sandstones is somewhat more variable and depends on adjacent rock types, the mineral composition of the sands and the depth of the aquifers (Davis and De Wiest, 1966). Evaporites dissolution can give rise to waters of very high salinity. The principle anions are sulphate and/or chloride while the principle cations are sodium and calcium, although this may vary depending on the nature of the evaporite (Drever, 1988).

A series of regional sequential changes can occur in dominant anions along flow lines as (Freeze and Cherry, 1979):

$$HCO_3^- \rightarrow HCO_3^- + SO_4^{2-} \rightarrow SO_4^{2-} + HCO_3^- \rightarrow SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-} \rightarrow Cl^-$$

(Chebotarev Sequence)

In large sedimentary basins, the Chebotarev sequence can be correlated with depth, and have been described in terms of three main zones (Freeze and Cherry, 1979):

(1) Upper zones of mainly HCO_3^- water low in TDS.

(2) Intermediate zones of higher TDS and SO_4^{2-} as the major anion.

(3) A lower zone with high TDS and a high concentration of Cl^-.

Thus, groundwater should evolve naturally from a bicarbonate facies in recharge areas to a sulphate or chloride dominated facies in discharge areas (Ophori and Toth, 1988). As the water moves progressively towards the discharge areas, the rate of increase of CO_3^{2-} + HCO_3^- decreases in favour of SO_4^{2-} which is acquired readily from bedrock strata (Ophori and Toth, 1988).

In the natural groundwater environment, the chloride content of the water normally increases gradually in relation with the residence time. Chloride can be regarded as an excellent tracer, such that it is a useful reference ion (Tredoux and Kirchner, 1981). In an unconfined aquifer, evapotranspiration primarily causes an increase in the chloride concentration of the groundwater due to the dissolution of sodium chloride. An increase in chlorinity depends on the availability of chloride in the host rock and the rate of groundwater circulation. Changes in the permeability of the host rock will affect the flow rate and thus also the chlorinity of the groundwater.

Groundwater generally has its lowest sodium percentage in and near the recharge area of the Auob Sandstone aquifer in Namibia (Tredoux and Kirchner, 1981). An increase in the concentration of sodium accompanies the decrease in the concentration of dissolved magnesium, calcium and potassium, the latter ions possibly being adsorbed on the interbedded and confining shales in exchange for the desorbed sodium ions (Tredoux and Kirchner, 1981). The decrease of the calcium and magnesium concentration in solution disturbs the equilibrium of the calcium-magnesium-carbonic acid-calcite system resulting in the dissolution of additional calcite (Tredoux and Kirchner, 1981). The calcium ions added to the solution are also exchanged for sodium, with the overall effect of these reactions being an increase in sodium, alkalinity and pH and a concurrent decrease of calcium and magnesium (Tredoux and Kirchner, 1981).

Talma (1981) found three distinct groundwater types on the basis of chemical and isotopic data, in sandstones, siltstone and shales intruded by dolerite dykes and covered by colluvium in the Beaufort Group near Venterstad. These are I. Recent (<20 years) Ca, Mg, HCO_3 water; II. Very pure, old $NaHCO_3$ water and; III. Old NaCl water with little Ca and HCO_3.

2.3.4 Stable isotopes (oxygen-18 and deuterium)

The differences in the isotopic composition of the groundwaters may be due to several factors. Factors that may control the isotopic variation in precipitation are (Mook, 1994):

(1) Temperature
(2) Latitude
(3) Altitude
(4) Seasonality

The processes responsible for changes in the oxygen-18 (^{18}O) and deuterium (^{2}H) concentrations relative to the global meteoric water line (GMWL) are indicated on a plot of ^{2}H vs. ^{18}O (Figure 4.2, p 45). The effect of processes such as evaporation before infiltration, CO_2-exchange, condensation, hydration of silicates, H_2S-exchange and the exchanges occurring between rock minerals and the water, can be identified using these stable isotopes (Domenico and Schwartz, 1990).

The GMWL is determined from (Craig, 1961):

$$\delta D = 8(\delta^{18}O) + 10$$

where: 8 is a general constant

10 is the intercept called the deuterium (d)-excess

The δ notation (Weaver et al., 1996) is expressed as parts per thousand (‰) or permil.

$$\delta = [R_x - R_s]/ R_s \times 1000$$

where: R_x is the isotopic ratio of the sample

R_s is the isotopic ratio of the standard - VSMOW (Vienna Standard Mean Ocean Water)

2.3.5 Groundwater pollution

Pollution sources are animal wastes, human wastes, results of agricultural tillage and irrigation. The main nutrients that manifest pollution are nitrate, phosphorous, potassium and sulphate (Schot and Van der Wal, 1992; Tredoux, 1993). Potassium and sulphate ions are readily sourced from geological material (Hem, 1989). The geology, in the South African context, does not contribute significantly to the nitrate loadings of subsurface waters (Tredoux, 1993). Heaton (1984) states that the sporadic occurrences of high nitrate waters are a result of point-source pollution.

Animal and human wastes mainly contribute the pollutants nitrates and bacteria. Groundwater is automatically filtered so that pathogens are rare if not absent (Helweg, 1978). Mineralisation of natural soil organic nitrogen and leaching when a virgin veld is turned to tillage, is also a common source of nitrates in agricultural areas. Lynch et al. (1994) states that contaminants are mainly affecting the shallow groundwater sources.

2.3.6 Statistics in hydrogeochemistry

Several statistical computer programs are available today that can perform statistical analyses on large data sets in a very short time. The most common and readily available packages are STATISTICA, Statsoft and various geohydrological computer programs.

The most simplistic procedure for correlating multi-element hydrogeochemical data is, to produce a matrix which contains the correlations among all possible pairs of the elements being considered (Levinson, 1980). Two variables in a specific data set are correlated if a simple bivariate scatter plot of the data has a linear trend (Swan and Sandilands, 1995). Marked differences in correlations are due to dissimilar physico-chemical environments. Correlation matrices that are symmetrical contain the correlation coefficients for all pairs of selected elements. Correlation coefficients are a measure of the degree of linear correlation (Swan and Sandilands, 1995). The correlation coefficients are essentially the ratio between the covariance and the square root of the product of the variances (Johnston, 1989).

Factor analysis has proved useful as an aid in the interpretation of geohydrochemical data (Schot and Van der Wal, 1992; Usunoff and Guzman-Guzman, 1989). The purpose of factor analysis is to find groups of variables with shared common variances (Johnston, 1989). Factor analysis has several advantages over classical graphical approaches. It can be used to interpret neutral chemical species and non-chemical data (e.g. temperature, pH, Eh and pCO_2) and secondly, variations in ions in small concentrations (e.g. trace elements) are not masked by chemically similar ions in greater concentrations (e.g. Cl) in the data sets (Usunoff and Guzman-Guzman, 1989). Numerical values are assigned to each factor and can range from +1.00 to -1.00. These are commonly referred to as loadings, which are a measure of the extent to which each factor is associated with a particular value. Thus, if two loadings of the same factor have the same sign (either positive-positive or negative-negative) then they are positively correlated. If they have opposite signs then they are negatively correlated. Furthermore, R- and Q-mode analyses are applied in factor analysis. R-mode analysis describes the similarities between variables and Q-mode describes the correlations between sampling sites (Hitchon et al., 1971; Reeder et al., 1972). The data are usually rotated (varimax rotation) to reduce the factor loadings to a simple structure by placing the highest possible loadings on the fewest number of variables, while preserving the independence of each factor and reducing the complexity further by allowing the factors to become slightly correlated (Levinson, 1980). These new combinations are then examined for significance in terms of process, types of samples, geological and geochemical information (Rose et al., 1979).

CHAPTER 3

STUDY AREA

3.1 INTRODUCTION

The physical character of an environment plays an important role in the occurrence and the quality of groundwater. This chapter will try to give an overview of the physical factors in the area that may influence the quality of the underground water.

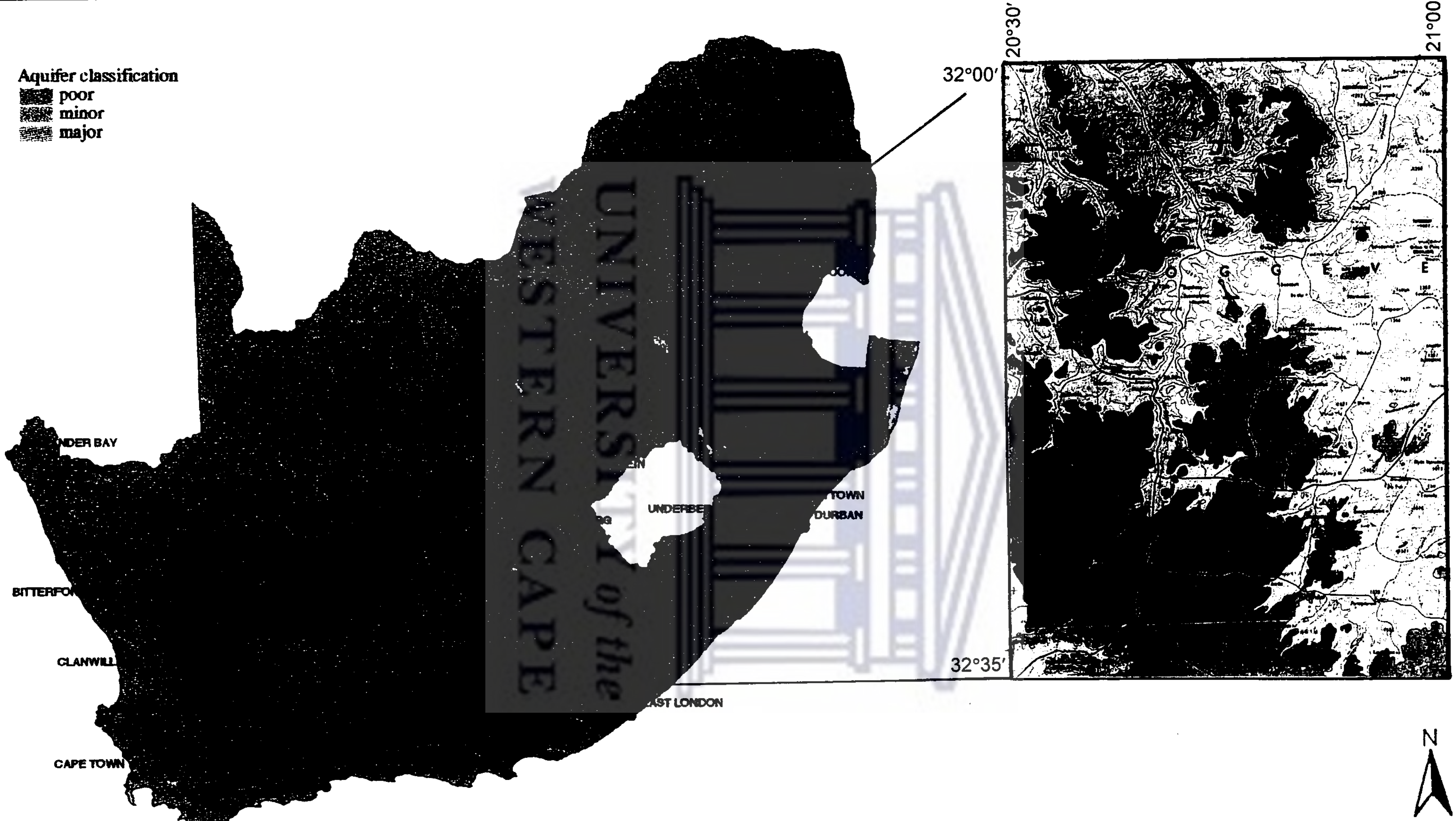
3.2 LOCATION AND EXTENT OF THE AREA

The study area is situated between 20°30′ to 21° 00′ E and 32° 00' to 32° 35' S (Figure 3.1). The study area incorporates the town of Sutherland in the Northern Cape Province. The area forms part of the Western Karoo region with an arid to a semi-arid climate. The study covers an area of approximately 3000 km^2. Undulating hills characterise the landscape. The hills are very often made up of doleritic intrusions.

3.3 CLIMATE

The climate of the Karoo is mainly determined by the degree of latitude, the distance from the sea and the height and topography of the area (Venter et al., 1986). The climate is influenced by a subtropical high-pressure belt, with a characteristic dry upper air layer (Venter et al., 1986).

With the exception of the southwestern parts, the major part of the Western Karoo receives mainly a summer rain, from October to March (Venter et al., 1986). The average annual rainfall decreases westwards from approximately 500 mm in the east to less than 100 mm over the northwestern areas. Over the high lying parts in the southwest, south and southeast, annual rainfall of up to 600 mm occurs. Venter et al. (1986) states that the average number of days per year with a rainfall of 10 mm or more ranges from approximately eighteen in the east to less than five in the west.



Sources: DWAF (1997) and topographical map 3220 – Sutherland.

Figure 3.1. Locality map of the study area.

The reliability of rainfall also diminishes from south to north. The mean annual rainfall in the Sutherland area is between 300-400 mm/year (Midgley et al., 1994). The amount of evaporation is between 1800 and 2000 mm/year (Midgley et al., 1994), almost six (6) times that of the precipitation. The amount of potential evapotranspiration increases from east to west (Simonis and Kok, 1989) and from south to north (Venter et al., 1986). Simonis and Kok (1989) found that the amount of potential evapotranspiration could be as high as 3000 mm in the west and Venter et al. (1986) give values of 1600 mm in the south to 2200 mm in the north. This factor is important especially with regards to the amount of rainfall that are available to replenish the groundwater sources in the area, since there is a definite relationship between the amount of rainfall and the water quality of a specific region (AEC, 1990). Areas experiencing very low rainfall generally have poorer quality groundwater as opposed to areas with higher annual rainfall.

Daily and seasonal temperature fluctuations in the Karoo are large and ranges of 25 °C between day and night temperatures are common. The mean daily minimum temperature is 3.9 °C and the mean maximum temperature is 20.3 °C for the Sutherland area. The mean annual temperature for Sutherland is 12.5 °C. The mean annual frequency of days with minimum temperatures below 0 °C for Sutherland is 80 and the frequency of days with maximum temperatures above 30 °C is 60 days (Venter et al., 1986). During the months of June, July and August, snowfalls occur over most of the study area.

3.4 VEGETATION

In the Sutherland area, Karoo and Karroid plants dominate (Acocks, 1988). The vegetation is sparse Karoo veld with stunted shrubs, especially in rocky areas and thornveld along the rivers. In the drier western part where the Great Karoo veld merges into that of the Little Karoo, *Tamarix usneoides* also become important along the rivers (Acocks, 1988). There exist little or no published information on the study area. A common feature of Karoo vegetation is that vegetation near water sources is much larger and greener than those found in dry areas. There is a close relationship between vegetation and fracture zones. A very good example of this phenomenon is the linear growth of the vegetation on fracture zones associated with dolerite or other intrusions, as well as along joints in the bedrock in which water is stored. The following vegetation types dominate the plant life in the area, namely rosemary, perdebos, bitterbos, harpuisbos, plakkies and renosterbos.

In an arid region such as the Karoo, water (i.e. rainfall, soil moisture and runoff) and evaporation is the most important environmental factor influencing the vegetation. Roux (1981) states that apart from the impact of the grazing factor, the Karoo vegetation exhibits significant fluctuations primarily because of the short-term shifts in seasonal rainfall.

Roux and Opperman (1986) found that the removal of the thin layer of topsoil, either by nature or by man, could be detrimental to the growth and reestablishment of plants. The topsoil cover is very shallow. However, soils tend to increase in thickness along rivers, valleys and the flatter plains in the north of the study area. The amount of soil cover is important in determining the amount of CO_2 available for the weathering of minerals in the unsaturated and saturated zones.

3.5 DRAINAGE

Non-perennial rivers drain the study area. These rivers only flow during periods of peak rainfall and are responsible for recharge of underground water. Farmers usually dam these non-perennial rivers for irrigation and stock watering. Dams provide a means of recharge to the aquifers, but due to the high evapotranspiration rates most of the water is lost to the atmosphere.

The main non-perennial rivers found in the area are the Sak River, Fish River, Roggekloof River, Riet River, Portugals River and Renoster River. These rivers mostly flow in a northerly direction.

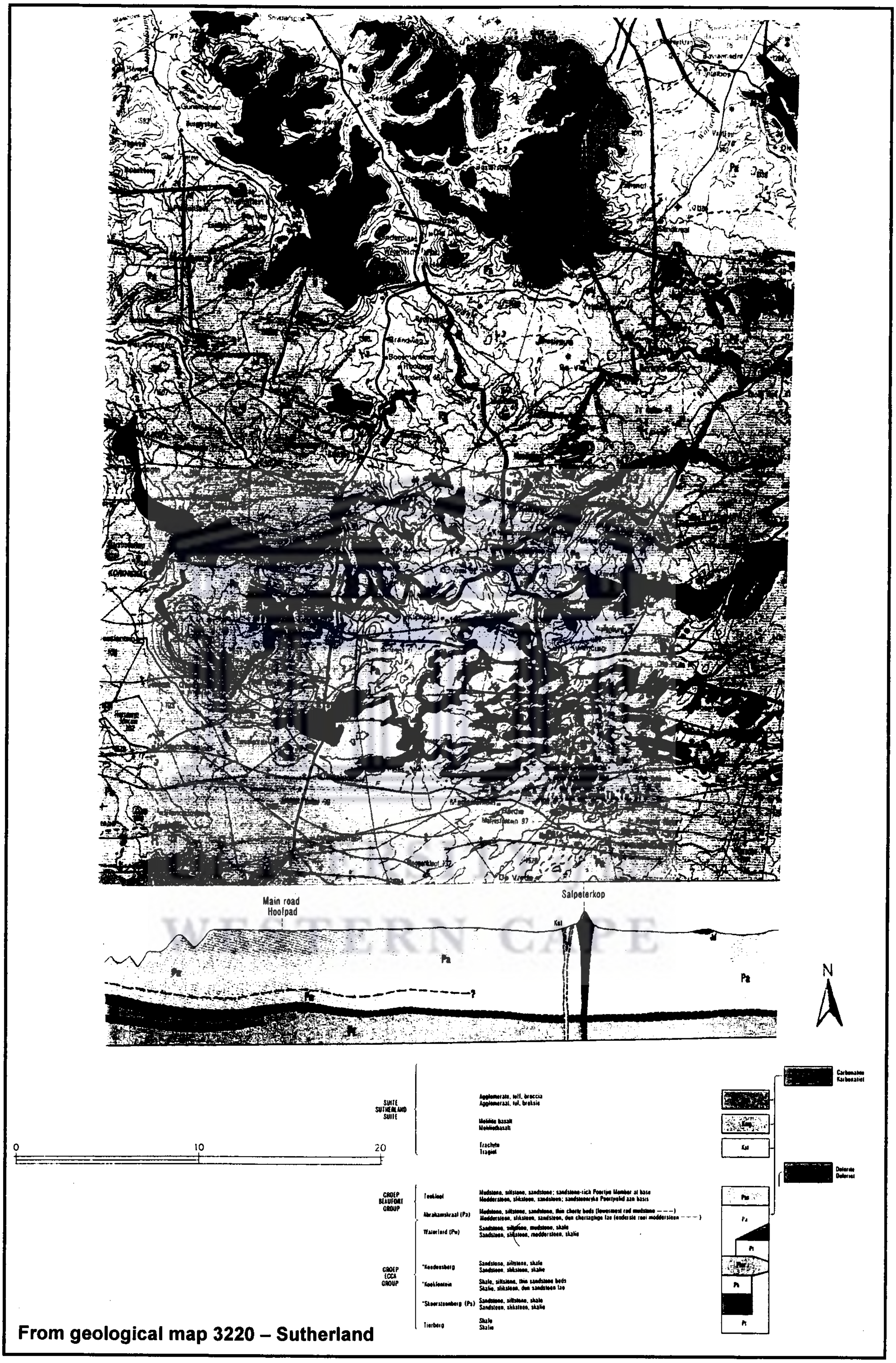
The runoff depends on the annual precipitation, the frequency of it, the topography, the nature of the soil and the geology of a specific area. Runoff is greatest in areas of high relief and along human induced pathways such as roads. Runoff only commences when the requirements of interception, surface retention and initial infiltration have been met. Midgley et al. (1994) gives values of about 10-20 mm per annum for runoff for the area. The amount of rain retained over the course of the year is a function primarily of the frequency of the showers, catchment gradient, the nature and density of the vegetation, vegetation controls interception and retardation of runoff.

3.6 GEOLOGY

3.6.1 Introduction

The main Karoo Basin covers an area of just over half a million square kilometres and basin fill took place from the late Carboniferous (280 Ma) to early Jurassic (100 Ma) (Visser et al, 1980). The Karoo Supergroup lies conformable on the Cape Supergroup of rocks that in turn lies unconformable on the Precambrian rocks (consisting of Malmesbury beds intruded by younger Cape granites) (De Wet, 1975). The Karoo sequence in the western half of the basin has a maximum thickness of about 6400 m along the southern margin, but thins rapidly northwards to an approximate thickness of 1000 m (Visser et al., 1980). Within the main Karoo basin, the Beaufort sediments follow the Ecca series conformably (Table 3.1). The geology of the study area mainly consists of the intercalated and arenaceous sedimentary rocks of the Beaufort Group and the two igneous intrusive phases during the early Jurassic and Cretaceous (Figure 3.2). The sediments are almost flat lying with dips between 2° - 3° to the north and northeast.

The sedimentary rocks are sandstones, shales, siltstones and mudstones, belonging to the Beaufort Group (Adelaide Subgroup) (Plate I, p112). Theron (1983) estimates the thickness of the Abrahamskraal Formation to be 1000 m in the Sutherland area. Outcrops of the Teekloof formation occur to the north of Sutherland. Except for the absence of limestone bands and chert layers the Teekloof formation does not differ that much from the underlying Abrahamskraal formation (Theron, 1983).



From geological map 3220 – Sutherland

Figure 4.2. Geological map of the Sutherland area.

The sediments were intruded mainly by east-west trending basaltic dolerite dykes and sills during the Jurassic, which exploited weaknesses in the sedimentary structures. Dolerites only begin to appear north of the folded foothills of the Cape Orogeny (Winter and Venter, 1970). The majority of sills is inclined, according to Du Toit (1954), and transgresses across the bedding planes with dips of 15-50 degrees being most common. Their outcrops tend to produce chains of hills that rise above the flatter ground built of sediments of the Karoo Supergroup. Du Toit (1954) also states that faulting may occur along these intrusions and that the dykes may merge with sills or it may cut the latter. The sediments in contact with intrusions invariably exhibit a certain amount of alteration, which increases with the thickness or width of the intrusion. During the Cretaceous the carbonatites and associated intrusions of the Salpeterkop Carbonatite Complex (SCC) intruded the sediments. The SCC is characterised by a ring complex with ultrabasic plugs and dykes (De Wet, 1975).

3.6.2 Lithology and mineralogy

3.6.2.1 Sandstone

Several types of sandstones are evident in the study area. Firstly, a greyish fine to medium grained type and secondly, a yellow-brownish medium to coarse grained variety.

Theron (1983) described a third type of sandstone as being a cross-layered blue to green-greyish sandstone that varies laterally in thickness (0.1 - 10 m). The sandstones mainly comprise of quartz, feldspars (orthoclase and albite plagioclase) and accessory minerals (biotite, chlorite, muscovite and calcite). Sandstone layers may attain a thickness of 30 m in the Sutherland area (Theron, 1983). The sandstones in contact with igneous intrusions are baked and tend to be harder and fractured. The sandstones tend to deform in a brittle fashion and thus the intensity and density of fractures are high.

Table 3.1. **Stratigraphy of the Karoo Supergroup as found in the study area, prior to the intrusions of dolerite dykes and sills and the Salpeterkop Carbonatite Complex (Cole et al., 1990; De Wet, 1975; Haughton, 1969; Smith, 1990).**

PERIOD	GROUP	SUBGROUP	FORMATION
JURASSIC -190my-	STORMBERG°		
TRIASSIC		TARKASTAD°	
-225my-	BEAUFORT (3000m)	------------------	---------------------------
PERMIAN		ADELAIDE	TEEKLOOF ABRAHAMSKRAAL
	ECCA (1800m)		WATERFORD# KOEDOESBERG* KOOKFONTEIN* SKOORSTEENBERG* TIERBERG WHITEHILL *(not exposed)*
-270my- CARBONIFEROUS	DWYKA (600m)		*Not exposed in study area*

*Not yet approved by SACS. °Do not occur in the study area.

3.6.2.2 Shales, mudstones and siltstones

Shales are not so common in the study area, but they have been observed in some localities. The shales are not very extensive or thick as in the case of the sandstones. The mudstones are predominantly massively layered, blue green in colour with alternating purple-red bands (Theron, 1983). These mudstone layers are made up of predominantly quartz and calcite. Siltstone outcrops are sparsely distributed.

3.6.2.3 Dolerite

Dykes of more than 25 km long are common (Theron, 1983) and transects the whole study area. Dykes may join with sills reaching thickness' of 150 m (Theron, 1983). Dolerite dykes and the fractures associated with them strike in all directions and tend to increase in abundance in the northern part of the study area. Theron (1983) states that there was more than one or else a very long continuous intrusive phase, because dolerite dykes intruded into the sills at most places.

The dolerite bodies that are younger than the folding is not completely concordant, but follow more or less the structural pattern (Theron, 1983). The sills follow an east-west trending outcrop pattern, while the dykes have a northwesterly strike. The sills outcrop for several kilometres and then suddenly pinches out and/or go over into a dyke which after several kilometres can join again at another sill (Theron, 1983). The sills readily outcrop as ring structures. The dolerite is a melanocratic, medium grained rock with an ophitic texture in which felspathoids and pyroxenes can be distinguished, sometimes porphyritic with felspathoids of 2.5 mm long (Theron, 1983). Generally, pyroxene occurs as bundle aggregates. Small amounts of magnetite and biotite also occur. According to Du Toit (1954) the dolerites are composed mainly of plagioclase and augite in about equal volumes. In the thinner sheets and in the dykes the texture is porphyritic with the crystals of plagioclase, pyroxene and olivine being embedded in a fine-grained matrix (or mesostasis) of pyroxene granules and feldspar microliths.

3.6.2.4 Melilite basalt and associated pyroclastic rocks

These rocks occur mainly in a linear zone, which strike east-west from Salpeterkop, past Sutherland to the western part of the area. They also occur in a series of dykes and plugs that occur in the Salpeterkop vicinity and to the west of Sutherland (Theron, 1983). Salpeterkop is a conical peak (1766 m above mean sea level) with a height of 250 m above the present land surface. Figure 3.3 shows the geological map of the Salpeterkop structure and an inferred cross section of the structure along A-B.

The Sutherland diatreme is found some 20 km southeast of Sutherland and comprises a variety of post-Karoo intrusive alkaline rocks (Newton, 1987) that also post-dates the Karoo dolerites (De Wet, 1975). These rocks are part of a group of extrusive and intrusive rocks comprising of pyroclastic rocks, potassium-trachyte, carbonatite, biotite-metacarbonatite and olivine melilite (De Wet, 1975).

Newton (1987) describes the diatreme as being associated with the warping accompanying the opening of the south Atlantic. He also found that it is later than the local post-Karoo dolerites. The Sutherland diatreme is at the focus of an imperfect, but clear radial pattern and with this is combined a very strong northeast trend and additional north-northwest and east-west fractures that are spatially not part of the radial system (Newton, 1987). The influence of this intrusion can be seen as far as 40 km away from Salpeterkop.

The pyroclasts range from coarse breccia to uneven layered yellow brown tuff. The clastic material consists mainly of Karoo sediments, fragments of quartz, dolerite, granites and gneiss fragments cemented by silica and iron oxides (Theron, 1983). De Wet (1975) found that all these rocks correspond in their content of minor elements viz. Ba, Sr, Nb, rare earths and Ti, a suite characteristic of that of carbonatites. This conclusion is corroborated by the presence of the minerals pyrochlore, barite and fluorite (De Wet, 1975).

3.6.3 Structure

The whole area is not greatly deformed and the folds that do occur, decrease in intensity in a northerly direction (Theron, 1983). The southern part still shows the influence of the Cape Fold Belt and has an east-west striking fold axes (Theron, 1983). Shallow folds and undisturbed horizontal layers are common, according to Theron (1983), but may be altered by narrower strips where steeper gradients occur. Although the fold axes dip at a low angle to the east- and westwards, the total effect is directed eastwards so that higher stratigraphic units occur more in this direction (Theron, 1983). Further deformation is restricted to the effects of the dolerite and pyroclastic rocks.

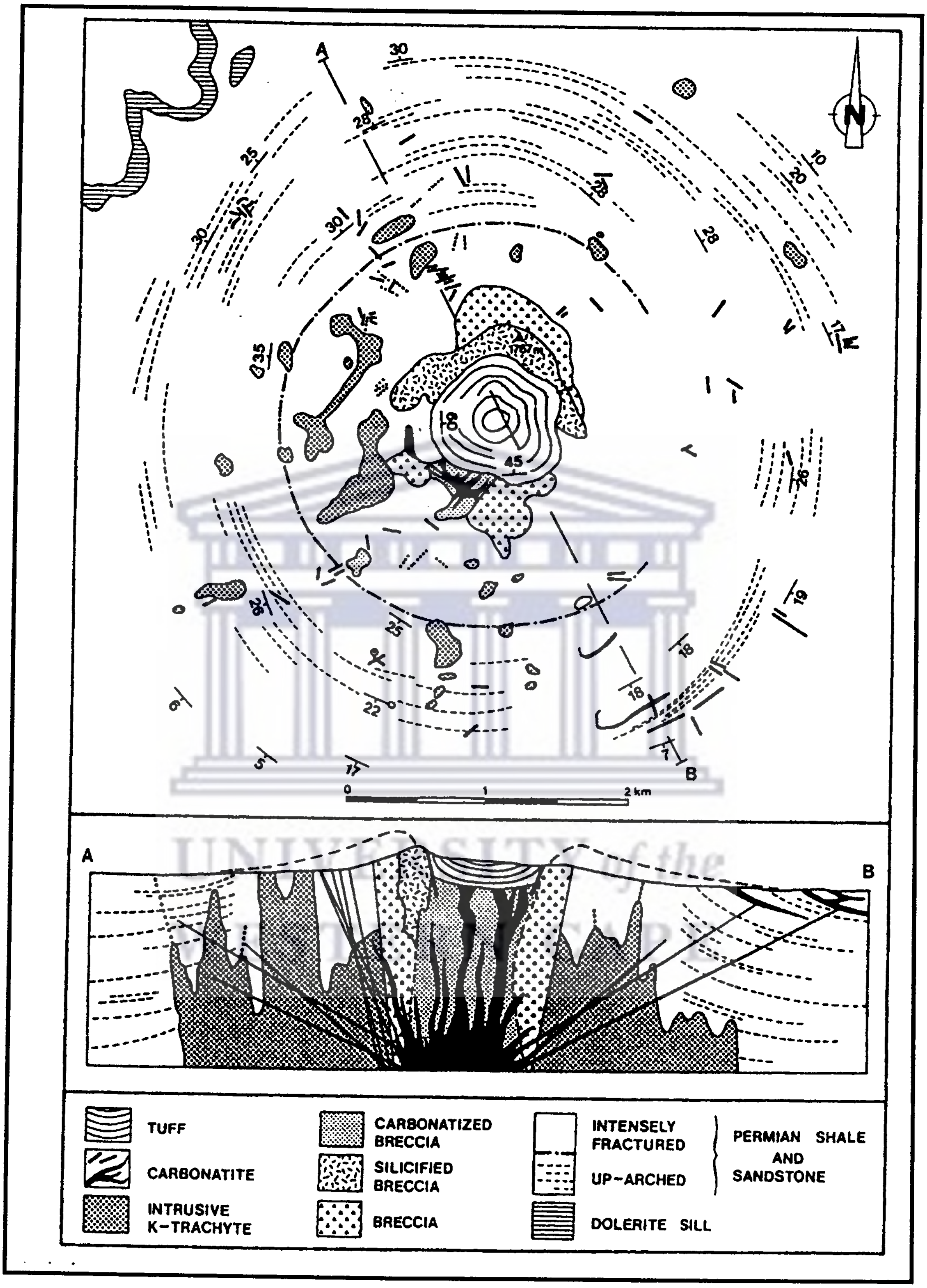


Figure 3.3. Plan view of the Salpeterkop Carbonatite Complex and inferred cross section (After Verwoerd, 1990).

Newton (1987) states the stress direction varies smoothly from north-south to north-northwest and that fracturing is related probably to the sub-Karoo rocks, i.e. the Cape Supergroup. The gentle folds in the Karoo rocks are interpreted as mainly due to settlement and compaction rather than orogenic stress, except in the south (i.e. just to the north of Sutherland), where the regular east-west folds are attributed to the persistence of the Cape Folding stresses into Beaufort times (Newton, 1987).

Despite the great thickness of the Karoo sediments and associated dolerites, which probably modified the pattern, the fractures propagate up through the Karoo from the Cape "basement" and reflect the stresses deforming the Cape rocks (Newton, 1987). In support of this contention, there is little evidence of any post-dolerite strain or present-day stress in the Karoo rocks. The diatreme occurs very closely to the intersection of major northeast, north-norteast, nortwest and east-west fractures suggesting that its location was structurally determined and that therefore these fractures were already in existence at the time of the intrusion (Newton, 1987). Each of these lineaments is at least 200 km long and probably extends down into the Precambrian basement, which is only some 4 km deep in the Sutherland area (Newton, 1987). On a Landsat image, according to Newton (1987), the average length of fractures is about 20 km with lengths of 30-40 km being common. It is thus feasible, even likely that these penetrate both the Cape and Karoo covers. The pattern over much of the western Karoo is that deformation is minimal, the cover thin and fractures must be largely due to upward propagation from the basement (Newton, 1987).

3.7 GEOHYDROLOGY

Groundwater is mainly found in the fracture and joint systems in the study area. In the absence of fractures, the sedimentary rock units do not constitute reliable aquifers. This is due to the poor hydrological properties (e.g. low permeability) of the sandstones. Fractures due to dolerite intrusions are common in Karoo aquifers and has been proven that their location is associated with relatively high yielding boreholes due to the fracturing they have caused in the adjacent country rocks (Robins, 1980).

The influence of the Salpeterkop extrusive complex also yields complex fracture systems that are pronounced around the ring structure. The effect of the Cape Orogeny to the south of the area also contributes major joint systems to the fractures of the area. Jointing is common along intrusive contacts and they are particularly valuable on the upslope side of the hydraulic gradients in the Karoo sediments (Robins, 1980). In the Strydenburg area Weaver et al. (1993) found that not all dolerite contacts yield water.

The bulk of the groundwater is stored in the matrices of the country rocks and the fractures serve as conduits for groundwater flow (Kirchner and Van Tonder, 1995). Impermeable barriers, especially doleritic dykes or sills, which limit the horizontal and vertical extent of the aquifers, may limit groundwater flow. These may be negative (i.e. impermeable) or positive (i.e. permeable) recharge boundaries and both types of boundaries may be present in one area (US Department of the Interior, 1981).

Groundwater generally moves from levels of higher energy to levels of lower energy, and its energy is essentially the result of elevation and pressure (Davis and De Wiest, 1966). The dykes and/or sills that transect the study area causes disruptions in the groundwater flow patterns resulting in the damming of the water on the upslope side of the barriers. The groundwater levels in the area may not always follow the general topography of the area and the water level at a borehole would thus resemble the amount of fractures penetrated, the continuity, spacing and the interconnectivity of the fractures/joints. The groundwater level would thus be a piezometric level and not always a water table. Artesian wells are also found in the area. Two of these boreholes have been observed on the farms Jakkalsvlei and Eseljacht, the latter being an unusual artesian well that discharges at a constant rate since it was drilled (Plate II, p112). According to Wilke (1962) the requirements for such artesian conditions are:

(1) A pervious aquifer to permit the entrance and passage of water.

(2) Confining upper and lower strata.

(3) That the borehole headlevel must be below the hydrostatic pressure surface of the water in the aquifer.

All the above requirements are met for the artesian wells found in the area. In the Eseljacht case dolerite layers prevent the escape of water upwards or downwards.

CHAPTER 4

METHODOLOGY AND CONCEPTUAL MODELS

4.1 INTRODUCTION

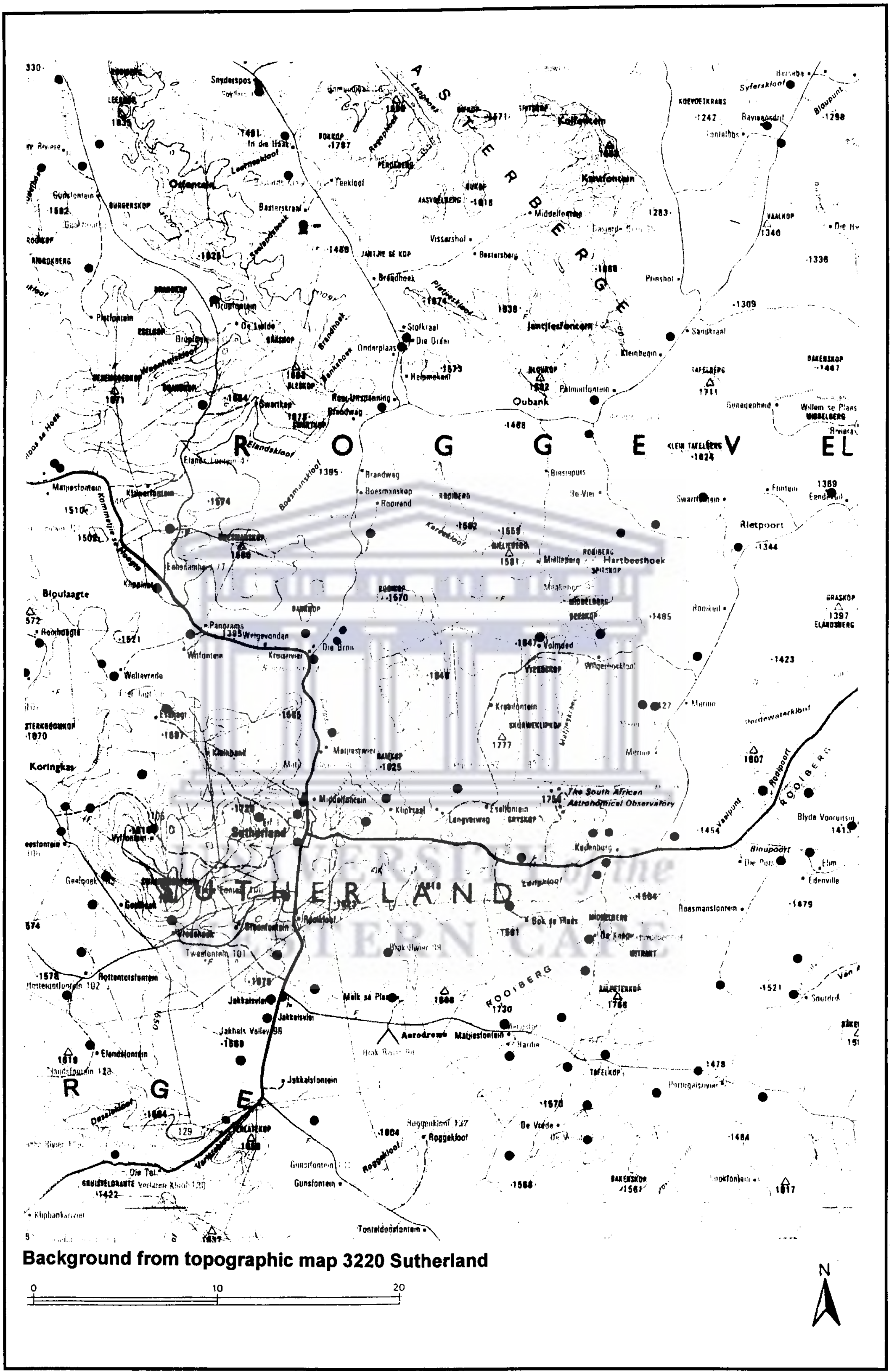
Gathering of data for this study was conducted intermittently between June 1996 and May 1997. All samples were analysed at the laboratories of the CSIR (Stellenbosch), Infruitec (Stellenbosch) and the Geochemistry Department at the University of Cape Town. Conceptual models are presented to try and define the factors that may impact on the groundwater chemistry.

4.2 METHODOLOGY

4.2.1 Sample localities

This study was conducted in the form of a hydrocensus whereby 300 boreholes were visited and 110 boreholes sampled for chemical analyses. The coordinates of all boreholes visited were determined with the aid of a Magellan Global Positioning System (GPS) with an accuracy of ±12 m. Figure 4.1 shows the spatial distribution of the boreholes visited during this study. The 110 boreholes sampled for chemical analyses were selected by looking at the drastic changes in electrical conductivity over short distances, the type of structures it was drilled on and the topography of the area. Twenty-two (22) localities were identified for isotope sampling. For these localities, identifying sites equipped with electric or fuel pumps was important because their capacity to draw water from deep and wide and because their capacity to remove stagnant water much faster.

Where windpumps were chosen for sampling, allowance was made for pumping for a significant period. Specific localities were also chosen intentionally, such as areas where ponding occur and areas that were geologically different.



● **Borehole positions**

Figure 4.1. Locations of all boreholes sampled for chemical analyses.

4.2.2 Sampling methods

Sampling procedures were according to those set out by Weaver (1992). All boreholes were pumped for a significant period to purge the boreholes of all stagnant water before sampling proceeded. Purging of the boreholes was essential since most of the boreholes visited were equipped with windpumps. All samples were filtered with a hand held syringe through a 0.45 µm filter membrane in the field. Samples were collected in two new 100 ml polyethylene bottles. All water bottles were washed with deionised water and again twice with filtered sample water. The samples were kept cool on ice in a cooler box before being dispatched to the laboratories.

Parameters that were immediately measured for at the time of sampling were alkalinity, pH, temperature, electrical conductivity (EC) and redox potential (Eh). These parameters had to be measured at the time of sampling because it may alter as a result of aeration and degassing (Parker, 1994). It also provides a preliminary overview of the water quality, which determined the extent of sample collection (Weaver et al., 1996). Portable pH and EC meters were used. All portable meters were calibrated at the beginning of each day and properly washed with deionised water after every sampling occasion. The determinants required for the study are outlined in Table 4.1.

Table 4.1. Physical and chemical determinants.

Group	**Determinants**
Physical determinants	EC, pH, Temperature, Eh
Major cations	Na, Mg, Ca, K
Major anions	Cl, SO_4, NO_3, F, HCO_3
Trace elements	Al, Ba, Ni, P, Sr, B, U, Cu, Mn, Zn
Isotopes	^{18}O, D
Aggregate determinants	Alkalinity

Two unfiltered samples were taken for isotope analysis in new 250 ml polyethylene bottles and properly sealed. A back-up sample was needed in case of leakage or contamination of one of the samples. All samples were kept cool during the period before despatching to the laboratory.

4.2.3 Laboratory analyses

Chemical analyses of the water samples were undertaken at the laboratories of Infruitec (Soil Science Section). The laboratory of the CSIR (Stellenbosch) was used to analyse for NO_x - N and F, and for quality control, some duplicate samples were sent to this laboratory to corroborate analyses done by the laboratories of Infruitec. Duplicate samples were also sent to the Infruitec laboratories for quality control. Isotope analyses were done at the Geochemistry Department of the University of Cape Town. Analyses for the stable environmental isotopes deuterium (D or ^2H) and oxygen-18 (^{18}O) were performed there.

4.2.4 Quality control

To determine the accuracy of the laboratory analyses duplicate samples were sent to two different laboratories using different analytical techniques. Duplicate samples were also sent to the same laboratory. Where the ionic balances were high, the samples were re-analysed and corrected.

4.3 CONCEPTUAL MODELS

Three conceptual models are proposed for the study area. These models would normally interact in nature. However, the models would be formulated separately to conceptualise the influence of the geological, recharge and topographical factors on the chemistry of the groundwaters. The models would be tested in Chapter 5 to ascertain if any of these factors contribute to the chemical character of the groundwaters in the study area.

4.3.1 Model I - Geology

4.3.1.1 Influence of the lithology on the groundwater chemistry

The weathering of rocks is both a chemical and mechanical process. The weathering process entails the interaction of an aqueous solution with rock material to produce a solution of different composition from the reactant one (Henderson, 1986). Precipitation with carbonic acid from biological processes in the soil, attack minerals and release dissolved components to the water (Katz and Choquette, 1991).

Percolation of water in the Karoo rocks is largely limited to the fracture and joint systems. The porosity of the rock determines the degree to which a rock will be chemically attacked because porous rocks are more penetrable by water. Furthermore, fine grained minerals are more susceptible to chemical weathering than coarser grained rock due to the larger surface exposed and because a protective residual coating develops around larger mineral grains, thus preventing any further chemical reaction between the unaltered surface of the grain and the water (Tordiffe, 1978).

Typical rocktypes found in the Sutherland area are a variety of sandstones, mudstones, shales, dolerites, carbonatites and melilite basalts. However, the main outcrops observed during the study are sandstones, dolerites and mudrocks. A major problem experienced was the lack of geological information. The rock forming minerals contribute to the chemical composition of the subsurface waters due to its reactivity to the hydrosphere. Weathering reactions between natural waters and the rock forming minerals that constitute the geology of the area, is the major geological control on the groundwater chemistry. The weathering of minerals is of importance for two reasons (Bricker and Jones, 1995):

(1) The weathering reactions determine the major dissolved species that occur in natural waters and,

(2) Trace elements commonly occur in solid solution in rock forming minerals and are released when these minerals are exposed to weathering.

Saturation indices (SI) calculated using the NETPATH, through a WATEQF subroute, (Plummer et al., 1992) software, show the degree to which a mineral has dissolved in water. If the saturation index is equal to zero, in the logarithmic form, the reaction is at equilibrium and the water is thus saturated with respect to the specific mineral (Freeze and Cherry, 1979). Where the SI value is negative, the water is undersaturated and if positive, the water is oversaturated with respect to any specific mineral.

The compositions of selected elements for various rocktypes are tabulated in Table 4.2. These estimates give a general picture of the distribution of elements among the major rocktypes found in the Karoo.

Table 4.2. Average trace element composition (ppm) of the major rocktypes (Chevallier (pers. comm.), De Wet (1975), Verwoerd et al. (1995)).

Element[1]	Dolerite	Carbonatitic breccia/dyke	Sediments
Ba	1154	6377/3135[2]	838
Cu	70	27	5.2
Ni	55	91	32.4
Sr	249	1674/613[2]	368
U	0.8	not detected	2.6

[1] Elements available and used in this study. [2] Values for dykes.

4.3.1.2 Influence of the fracture systems on groundwater chemistry

Several fractures in the area have been identified and discussed by Newton (1987). The fractures have been extensively mapped by the Geological Survey from Landsat and aerial photos on a scale of 1:50 000.

The fractures are usually associated with a certain tectonic event such as the intrusions of the dolerites, carbonatites and kimberlites in the Karoo (Plate III, p113). The effects of the Cape Orogeny can also be observed by the major joints in the area. These fracture patterns are usually targeted by farmers for the siting of boreholes. Fractures are sometimes easily identified in the field by the linear growth of greener and larger vegetation on these fractures. Newton (1987) postulated that the fractures penetrate the Cape basement and Karoo covers and that their lengths can vary from a few metres to several kilometres. Intersections of different fractures are common.

If the chemistry of the water at any point is characterised by the fracture drilled on, the chemistry of that water would be similar at another point where the same type of fracture occurs. Where the groundwater chemistry show no correlation with the fracture type, the fractures would then only serve as high conduit units and would thus be associated with the quantitative aspect of the groundwater. The aspect of quantity falls beyond the scope of this study. Fractures that may be significant are those associated with the dolerite and carbonatite intrusions. The reason being that dolerite and carbonatite intrusions occur along these fractures. Whereas, the fractures associated with the kimberlites and those associated with the Cape Orogeny (i.e. major joints) is not infilled by these rocktypes/material and may only represent a break in the rock formations.

4.3.2 Model II - Recharge

The area receives precipitation as rain, snow and mist. The precipitation is mainly derived from moisture from the Atlantic Ocean. The groundwater is replenished during these precipitation events. Recharge would then mainly occur at intrusive contacts of dolerites or where the fracture and joint systems are exposed at the surface.

The chemistry of precipitation is ideally the initial water source available for recharge. As the precipitation moves through the air and reaches the soil surface, it would have undergone chemical changes due to various processes. During the infiltration of these CO_2 charged meteoric waters, chemical reactions between the water and the soil and rock occurs resulting in the solution of anions and cations (Tordiffe, 1978). In the unsaturated zone above the groundwater level the precipitation of salts may occur. Once the precipitation has reached the soil and the infiltration capacity has been reached, overland flow and ponding occurs.

The usage of the environmental isotopes ^{18}O (oxygen-18) and D (deuterium) is gaining recognition in groundwater quality studies, especially replenishment of evaporated surface water. The depletion of these stable isotopes as they move away from their source, the ocean, can define several processes that determine the groundwater composition. Values for the ^{18}O and D of an area are plotted relative to a Global Meteoric Water Line (GMWL) or Local Meteoric Line (LML). If water with an isotopic condition fall on the GMWL it is assumed that it originated from the atmosphere and that it is unaffected by other isotopic processes (Domenico and Schwartz, 1990). Deviations from the GMWL indicate different processes affecting the ^{18}O and D ratio as depicted in Figure 4.2.

The replenishment of the subsurface waters would ideally start with a young Ca-HCO_3 type water and as the water interacts with its physical environment, it will change its signature to that of a Na-Cl type of water. So areas of higher topography would tend to have a more recent recharged type water (Ca-HCO_3) due to its low reactivity with its environment and where these waters are discharged or become more static the water chemistry would tend to evolve towards a more stagnant type water (Na-Cl).

4.3.3 Model III - Topography.

Changes in elevation of the land surface have a marked influence on the chemical quality of the waters. The changes in the chemistry of the water along a flow path depend on the initial water added to the aquifer at a given point. This water usually has a predominant HCO_3^- signature and as the water flows towards an area of discharge it acquires a more Cl^- rich character.

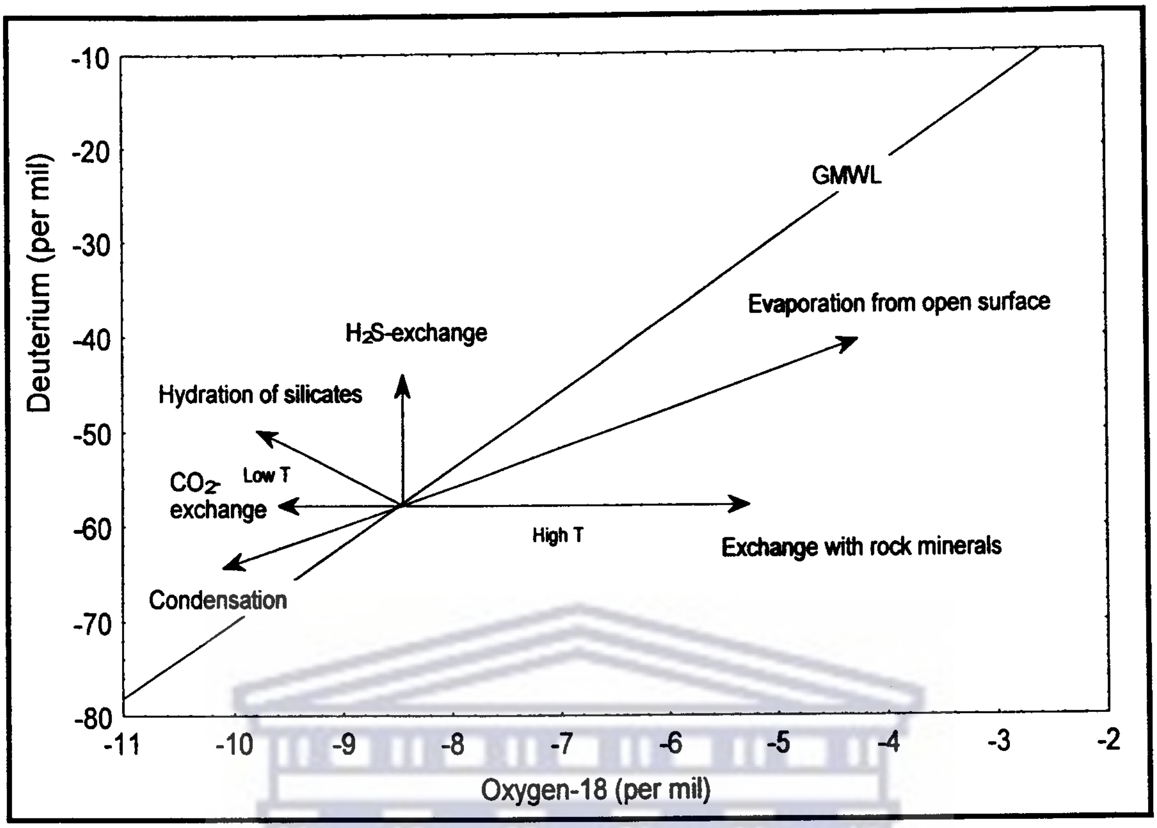


Figure 4.2. **D vs. ^{18}O diagram indicating processes that may affect the stable isotope ratios (modified after Domenico and Schwartz, 1990).**

As the water moves progressively towards the discharge areas, the rate of increase of CO_3^{2-} + HCO_3^- decreases and an increase of SO_4^{2-} is usually noticed which are readily acquired from bedrock strata. This sequence is commonly known as the Chebotarev sequence (Freeze and Cherry, 1979). The changes in the dominant anions along a flow line are as follow:

$$HCO_3^- \rightarrow HCO_3^- + SO_4^{2-} \rightarrow SO_4^{2-} + HCO_3^- \rightarrow SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-} \rightarrow Cl^-$$

The above sequence is also dependent on the residence time of the recharged water (i.e. the rate at which it flows away from the recharge area). During sampling, the areas in which boreholes are located have been classified as hills, foothills, valleys, rivers and flats. Generally, recharge occurs in areas that are flat, on slopes, in valleys, rivers and hills. However, the amount of time that the water is in contact with its surroundings will determine the amount of chemical constituents that will be added to the groundwater.

Water in higher lying areas will tend to move away to flatter areas due to the effects of the water gradients. Waters that occur in areas that are high lying have very low Cl^- values as opposed to areas situated in flatter areas or areas that acts as discharge points.

Evaporation and its relation to drainage are the major factor that influences the accumulation of salts. Generally, in flat areas where water, from precipitation, is allowed to pond the accumulation of salts is pronounced (Plate IV, p113). The effects of the high evapotranspiration rates are the main contributors in the accumulation of these salts. Sami (1992) stated that as evaporation exceeds precipitation throughout most of the year, leaching is limited and soluble salts tend to accumulate near the soil surface. Runoff and percolation periodically flush these salts into streams and the subsurface after large rainfall events.

These phenomena can be described by looking at specific flow lines in some specific areas or grouping of the boreholes in different topographical settings. This relationship between water quality and topography will be evident in mostly the major cations and anions as well as EC/TDS. The chemical changes that occur over time and space along a flow path can identify groundwater flow (from high to lower lying areas). Water in high lying areas will have a more bicarbonate type water and water in flatter areas a more salty type water (i.e. sodium chloride type waters). However, areas of recharge will also have a bicarbonate overprint within the waters that may occur in flat areas where chloride rich water is expected. Thus, the effects of mixing should also be incorporated in interpreting the data.

CHAPTER 5

HYDROGEOCHEMISTRY

5.1 INTRODUCTION

The hydrogeochemical data will be presented, analysed and interpreted in this chapter. Statistical analyses of the data set would be used to determine the major factors and processes characterising the groundwater around Sutherland. Several limitations influence the interpretation of the hydrochemical character of the groundwater. Firstly, the lack of adequate geological information and secondly, water level data and the fact that there were no control (i.e. borehole logs and data on water strikes) of the boreholes during sampling.

5.2 PRECIPITATION CHEMISTRY

Precipitation in the form of three rainwater samples and one snowmelt sample were collected in Sutherland during rainfall and snowfall events. The analyses are presented in Appendix I.

The rain and snowmelt samples collected were very dilute and moderately acidic with pH values of 5.2 and 6.1, respectively. The low pH of the precipitation samples is due to the dissolution of atmospheric CO_2 with water. This is characteristic of precipitation across the world. The total dissolved solids (TDS) concentrations vary between 8.45 - 24.15 mg/l. The rain water samples had high ionic balance errors in the order of 67-95% and very low TDS concentrations. The snowmelt had an ionic balance error of only 4.89%. Large ionic charge balance errors are common in dilute groundwaters with low total dissolved solids concentrations (Katz and Choquette, 1991). The snowmelt has high amounts of Ca, Mg, Na and SO_4 as opposed to the rainwater samples, which had in turn higher concentrations of Cl. These higher levels can be attributed to the dissolution of dust particles accumulating in the snow because of atmospheric fallout.

5.3 SURFACE WATER CHEMISTRY

Two river samples were collected from the Renoster River after a rainfall event. One sample (Rivbas) was collected from a tributary of the river and another sample (Renriv) from the main river. Data on the chemistry of these two rivers are presented in Appendix II. The rivers only flow in periods of significant rainfall. River water has, obviously, higher levels of dissolved solids compared to precipitation. The water from the tributary has its origin in the hills not far from the point of sampling. The main river flows over a large distance and is fed by smaller streams. As the water flows over the surface, it dissolves elements from the soils and chemically reactive rocks. The surface waters are further concentrated by the effect of evaporation. Thus, the chemistry of the water is already significantly altered before it is recharged into the subsurface.

The water from the main river has a much higher TDS concentration than that of the tributary. The concentrations of most of the elements were much higher than that of the tributary except for Ca, Mg and HCO_3. The water from the tributary was presumed to be water that was derived more recently from precipitation. This water was a Ca-HCO_3 type water while the water from the main river was a Na-HCO_3 type water. Water from the tributary also plotted closer to the recharge corner (Na+K/SO_4+Cl corner of diamond field) of the Piper diagram (Figure 5.1). The water from the main river plots towards the middle of the diagram. The usage of the Piper diagram for surface waters is justified because of the low flow rate of the rivers at the time of sampling. The Piper diagram is used for these two samples only to indicate the relative composition of the waters. The dominance of the Na - cation in the water of the main river was indicative of replacement (ion exchange) of Na for Ca. The tributary waters were not yet dominated by the effect of ion exchange. Changes in the chemistry of the surface water are indicative of a natural water evolution sequence, whereby the processes of ion exchange and concentration due to evaporation dominate the chemistry of the water.

5.4 GROUNDWATER CHEMISTRY

5.4.1 Statistical analysis

3 5.4.1.1 Introduction

A complete hydrochemical data set appears in Appendix III. The reliability of the data set was tested by charge balance calculations using only the major chemical parameters. Ninety percent (90%) of the data falls in the 5% ionic balance error range and 98% of the samples are in the 10% ionic balance error range. Only two samples showed anomalously high ionic balance errors. The two samples with the high charge differences were excluded from the data set.

Statistical analyses for the interpretation of large data sets are commonly used in geohydrochemical studies (Ashley and Lloyd, 1978; Dawdy and Feth, 1967; Usunoff and Guzman-Guzman, 1989). In order to get a clear understanding of the groundwater's chemical behaviour in the study area, a basic understanding of the chemical determinants or parameters must be gained. Applications of statistical techniques were a starting point from where more detailed interpretations and explanations were sought. Relationships between various chemical parameters were identified using statistics, specifically correlation matrices. Data reduction and classification were achieved using factor analysis. All statistical analyses were calculated using the *STATISTICA* software package.

The statistical approach applied in this chapter is as follows:

(1) The descriptive statistics give an overview of the average groundwater composition in the study area. The mean and ranges of the groundwater chemistry are compared with the mean composition of the rain samples found in the study area.

(2) In order to find any relationships between the variables in the data set the use of correlation matrices proved useful. Thus, a correlation coefficient matrix was produced as a measure of how well the variance of each variable can be expressed by its relationship with each of the other variables. The degree of linear correlation is termed the correlation coefficient, whereas the variances are a measure of the scatter of values around the mean.

(3) The data set was analysed using factor analysis (R-mode) to find the main factors or processes responsible for the groundwater chemistry in the area. Factor analysis is a tool used to rearrange data to present it in a manner that better explains the structure of the underlying system that produced the data (Dawdy and Feth, 1967). Thus, a set of factors is created in a simple structure to explain the interrelations of the chemical parameters.

5.4.1.2 Descriptive statistics

An overview of the descriptive statistics of the hydrochemical variables for the area is presented in Table 5.1. The pH of the groundwater ranges between 6.32 and 8.5, an indication that most of the dissolved carbonates are, predominantly, in the HCO_3 form (Domenico and Schwartz, 1990). Electrical conductivity (EC) and total dissolved solids (TDS) values vary between 40.6 - 986 mS/m and 131.68 - 5468.54 mg/l for the area, respectively. From the average composition, it is evident that the groundwater in the area is not uniform and differs considerably. In situ EC measurements indicated that the groundwater salinity changes over very short distances.

The groundwater chemistry varies considerably from that of the chemistry of rainwater (Table 5.1). An indication that several chemical processes occurred between the initial rain water chemistry and the final groundwater chemistry. The pH of the rainwater is much lower than that of the groundwater. This may be associated with the dissolution of carbonate minerals in the subsurface and a concurrent increase in the pH of the groundwater.

Table 5.1. Univariate statistical overview of the data set (rain and groundwater samples).

		GROUNDWATER				
Variable	**Rain (Mean)**	**Mean**	**Median**	**Min.**	**Max.**	**Std. Dev.**
pH	5.16	7.32	7.3	6.32	8.5	0.34
EC(mS/m)	1.49	159.4	133.4	40.6	986	119.6
Temp.(°C)	12.75	18.6	19.2	5.9	24.1	3.02
Eh(mV)	N.D.	-15.32	-15.7	-71.00	37.9	17.46
$p\mathrm{CO}_2$(atm)	N.D.	0.02	0.01	0.0003	0.05	0.01
Alkalinity	0.6	275	263	85	550	105.6
TDS	16.65	1053	939.9	131.7	5469	691.4
HCO_3	8.65	312.8	311.5	55.6	563.6	112.1
K	0.24	2.70	1.96	0.52	18.15	2.63
F	0	1.26	1	0.2	6.8	1.08
Cl	6.07	268.6	176.9	25.9	2923	348.5
Ca	0.26	107.2	89.7	11.81	633	79.90
SO_4	0.57	147.8	100	0	738.5	147.9
NO_3	0	4.74	0.22	0	37.2	7.49
Mg	0.16	40.02	32.1	4.15	351.2	40.36
Na	0.2	159.4	131.3	14.07	807.4	133.2
Sr	0.01	2.51	1.81	0.1	14.15	2.40
Al	0	0.02	0	0	1.26	0.12
Ba	0.002	0.08	0.06	0.01	0.63	0.07
Ni	0.02	0.01	0	0	0.23	0.04
P	0.08	0.1	0	0	1.19	0.18
B	0.003	0.27	0.18	0	1.72	0.30
U	0	0.09	0.08	0	0.7	0.09
Cu	0.004	0.01	0.001	0	0.1	0.01
Mn	0	0.06	0.01	0	0.82	0.13
Zn	0	0.1	0.02	0	3.37	0.35

All values in ppm unless otherwise indicated. N.D. = Not determined. Std. Dev. = Standard deviation.

5.4.1.3 Correlation matrices

Multivariate statistics were used, specifically Pearson's correlation matrices, to find any correlations between the different chemical constituents of the subsurface waters. Correlations are a measure of the relation between two or more variables (Levinson, 1980). Correlation matrices are useful tools in finding relationships between two or more chemical constituents in large data sets. Correlation coefficients (r) range from +1.00 (perfect positive correlation) to -1.00 (perfect negative correlation). A correlation coefficient of 0.00 would lack any correlation. Only correlations with $r > |0.4|$ are used. Samples with correlation coefficients of $\geq |0.7|$ shows strong correlations whilst correlations of $r = |0.5 - 0.7|$ has moderate correlations at a significant level of <0.05. Hydrochemical parameters with significant correlations are presented in Table 5.2.

Table 5.2. Pearson's correlation matrices for data showing marked correlations at a significance level of <0.05.

	pH	EC	Sr	B	Mn	F	Cl	Ca	SO_4	Mg	Na	HCO_3	K	Eh	pCO_2
pH	1														
^{1}EC		1													
Sr		.64	1												
B	.40			1											
Mn					1										
F	.64			.59		1									
Cl		.94	.75				1								
Ca		.81	.81		.40		.87	1							
SO_4		.59	.55				.54	.65	1						
Mg		.88	.52				.89	.81	.55	1					
Na		.83	.67	.50		.47	.82	.59	.63	.73	1				
HCO_3	.45											1			
K											.54		1		
^{2}Eh	-.91					-.59								1	
$^3pCO_2$	-.77											.45		.70	1

All values in ppm unless otherwise indicated (^{1}mS/m; ^{2}mV and ^{3}atm).

Very strong correlations exist between the major elements, Na, Ca, Mg, Cl with electrical conductivity (EC). These relationships clearly identify the main elements contributing to the groundwater salinity. Moderate correlations between SO_4 and Sr with EC also indicate that these elements tend to increase in concentration as the salinity of the water increases.

The salinisation of the groundwater may be the result of increasing concentrations of dissolved ions due to evaporation as well as the effects of interactions between the groundwater and the geological materials. If elements are released from the aquifer matrix, then the amount of cations released is matched by chloride. Waters high in salinity may thus be added to the subsurface before and possibly during events of recharge.

The contributions of evaporitic salts or salts in the geological material are possibly shown by the positive correlation between Ca-SO_4, Na-SO_4, Mg-SO_4 and Sr-SO_4. The most important evaporite present is that of $CaSO_4.2H_2O$ (gypsum). Gypsum deposits have been observed in the field where it was precipitated on fracture walls.

The major exchangeable ions Na-Ca, Na-Mg, Sr-Ca, Sr-Mg, Sr-Na and K-Na all correlates positively. Cation exchange processes are possibly a source of elemental concentrations in the groundwaters.

The negative correlations between pH, Eh and pCO_2 indicate that Eh and pH depends on the pCO_2 of the groundwaters. A decrease in pH is matched by an increase in pCO_2 and Eh. Redox potential (Eh) and pH diagrams are commonly used to determine the mobility of metals in groundwaters (Appelo and Postma, 1994; Hem, 1989). These correlations exist in natural groundwaters and can thus be a measure of the validity of correlation matrices in the interpretation of groundwater data.

5.4.1.4 Factor analysis

Interpretation of the factors is only a preliminary approach and would be tested with various other hydrochemical techniques. Factor analysis only shows the relationships between variables. The factors would be used to target specific correlations or relationships that are evident from the statistical analyses.

In the data set, factor extraction was carried out by means of principal components using the computer software *STATISTICA*. Varimax rotation, the most commonly used method of rotation, was used to obtain uncorrelated components (Schot and Van Der Waal, 1992). Rotations were used to find the maximum amount of factors (Drever, 1988).

The results of the factor analyses are outlined in Table 5.3. Component loadings that are $\geq |4|$ are included in the results.

Factor 1 is related to the largest eigenvalue and is able to explain the greatest amount of variance in the data (Usunoff and Guzman-Guzman, 1989). The second factor (factor 2) will then explain the greatest of the remaining variances and so forth.

Five (5) factors account for 76.22% of the variance (Table 5.3). Factor 1 is interpreted as mainly the salinisation of the groundwater due to the infiltration of evaporated surface water. The main contributors to the groundwater salinity are Cl, Ca, Mg, Na, Sr and SO_4. The main cation exchange elements Ca, Mg, Na, Sr are all positively correlated indicating the influence of the geological matrices. Significant correlations between Ca, Sr and SO_4 may show that the processes of dissolution or precipitation of evaporitic and sulphate minerals were taking place. The source of the SO_4 could also have been a result of redox reactions and the effects of land use practices. The salinisation of the groundwater mask the influences of other hydrochemical processes.

Factor 2 indicates the effect of pCO_2 on the pH and the known relationship (i.e. negative) between pH and Eh. These determinants seem to influence or regulate the mobility and solubility of the trace elements boron (B) and fluoride (F).

Possible pollution of the groundwater could be related to factor 3, with the correlation between NO_3 and K. Recently recharged water may be responsible for the flushing and leaching of NO_3 and possibly K to the groundwater system. The presence of HCO_3 within the factor is indicative of this phenomenon. Manganese (Mn) is probably related to weathering of minerals containing Mn.

Factor 4 may also be indicative of pollution through land use practices due to the presence of the elements P, NO_3 and K, which are principal plant nutrients.

Table 5.3. Results of principal component factor analyses with Varimax rotation.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
$pCO_2^{(1)}$		0.729			
pH		-0.922			
$EC^{(2)}$	0.922				
$Eh^{(3)}$		0.916			
HCO_3			0.783		
Ba					-0.799
P				0.871	
Sr	0.818				
B		-0.650			
Mn			-0.484		0.442
NO_3			0.611	-0.463	
Cl	0.955				
SO_4	0.719				
Ca	0.914				
Mg	0.865				
Na	0.838				
K			0.566	0.467	
F		-0.705			
Explained variance	5.649	3.400	2.066	1.441	1.165
Cumulative % of variance	32.69	51.28	63.50	70.61	76.22
Eigenvalues	5.88	3.35	2.20	1.28	1.01

All values in ppm unless otherwise indicated (^{1}atm; ^{2}mS/m and ^{3}mV).

Factor 5 is possibly the result of the water-rock interactions in the subsurface. Sources of barium in the groundwater could be the mineral barite ($BaSO_4$) and the rock forming mineral K-feldspar. These minerals are common in carbonatite rocks associated with the Salpeterkop Carbonatite Complex. Manganese is probably related to rocks containing the minerals olivines, pyroxenes and amphiboles (Hem, 1989). Small amounts of Mn are commonly found in carbonate minerals and may substitute for calcium (Hem, 1989). Thus, Mn can also be involved in cation exchange reactions involving carbonate minerals (Factor 3; table 5.3 and Mn-Ca correlation; Table 5.2).

5.4.2 Groundwater types of the study area

5.4.2.1 Introduction

Stiff diagrams were generated using Groundwater for Windows (GWW) to determine the main water types in the study area. The main cations and anions in a specific water sample essentially determine the dominant water types.

5.4.2.2 Groundwater types

The dominant groundwater types found in the area were the Na-Cl type water followed by Na-HCO_3 and Ca-HCO_3 types water and to a lesser extent Ca-Cl, Ca-SO_4, and Na-SO_4 waters. The different water types are depicted graphically in Figure 5.2. It is evident from the histogram that there is no dominant hydrochemical facies for the groundwaters in the Sutherland region. This assumption is evident from Figure 5.4.

Subdivisions of the Piper diagram on the basis of water types showed that the different water types plot more or less in different clusters. Identification of the water types in terms of regimes and recharge/discharge zones were accomplished using a composite Piper diagram depicted in Figure 5.3 (Kirchner, 1994; Ophori and Toth, 1988; Piper, 1944). Ophori and Toth (1988) associated cation-anion facies with either discharge or recharge zones, whereby facies 1 and 3 represents discharge zones and facies 2 and 4 with zones of recharge.

Kirchner (1994) and Piper (1944) associated zones on the Piper diagram with particular water types and regimes (Figure 5.3). The six different water types in the study area are described in terms of its relative positions to the zones described by Kirchner (1994) and Piper (1944).

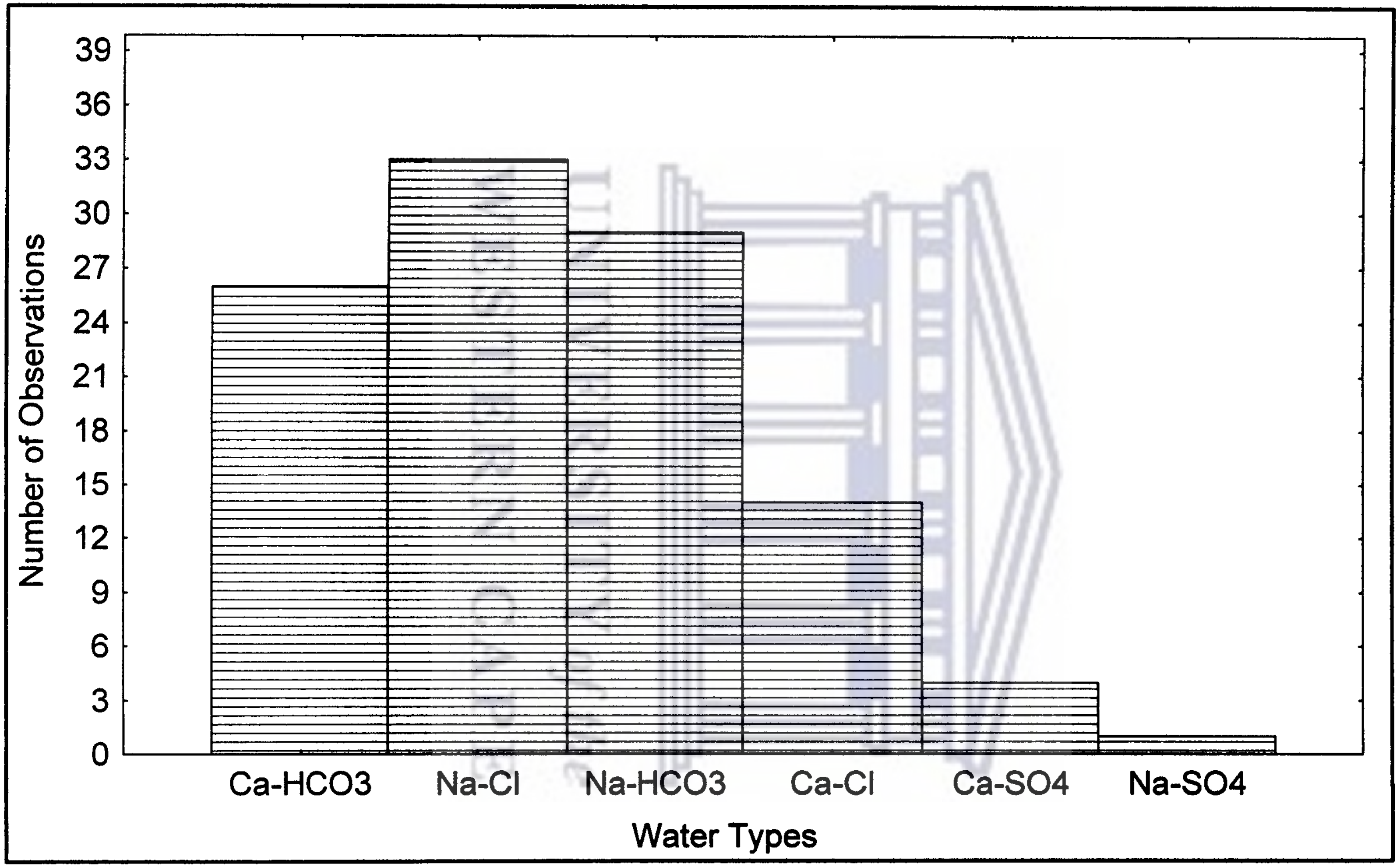


Figure 5.2. Histogram of the main groundwater types in the area.

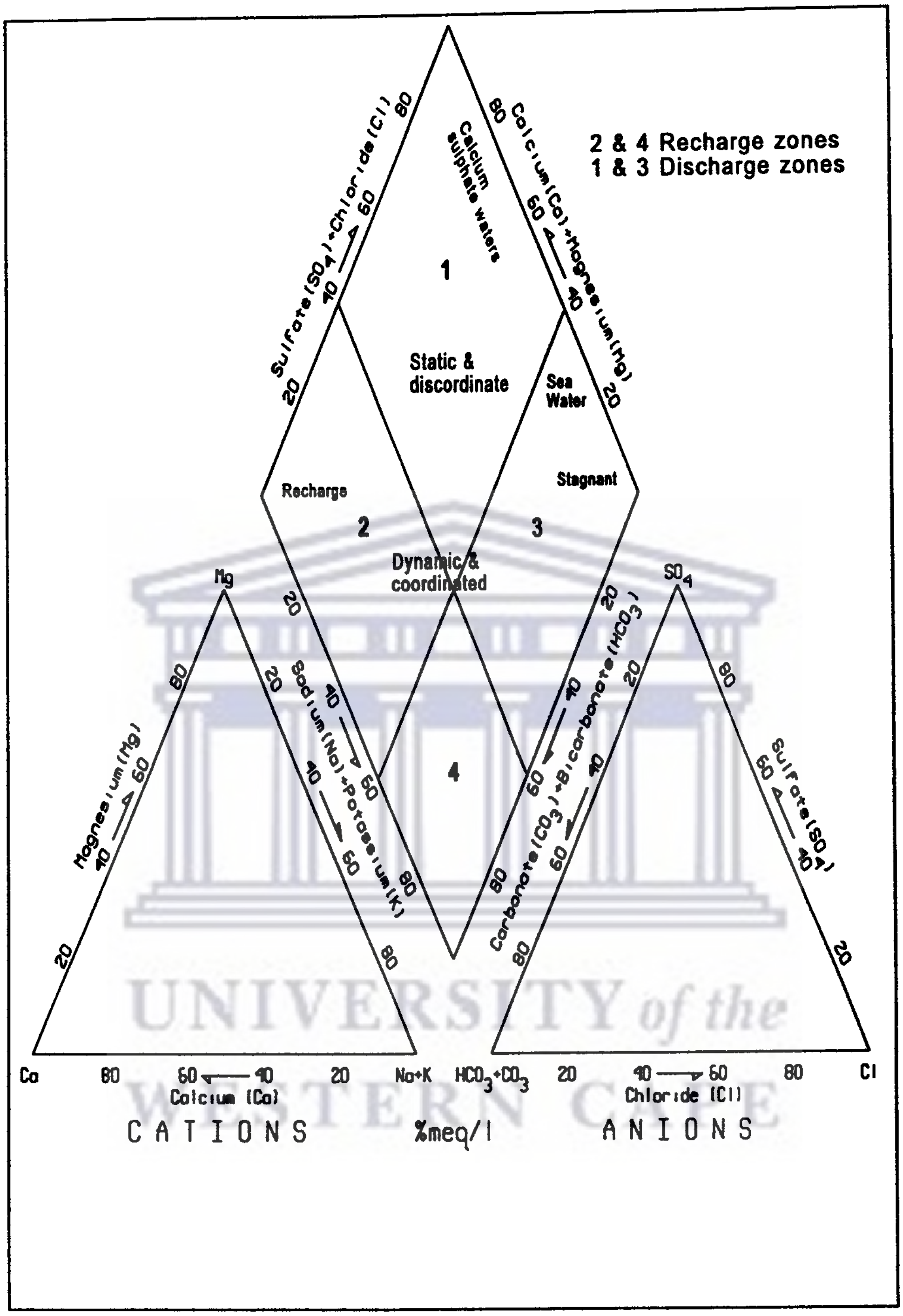


Figure 5.3. Composite Piper diagrams (Kirchner, 1994; Ophori and Toth, 1988; Piper, 1944).

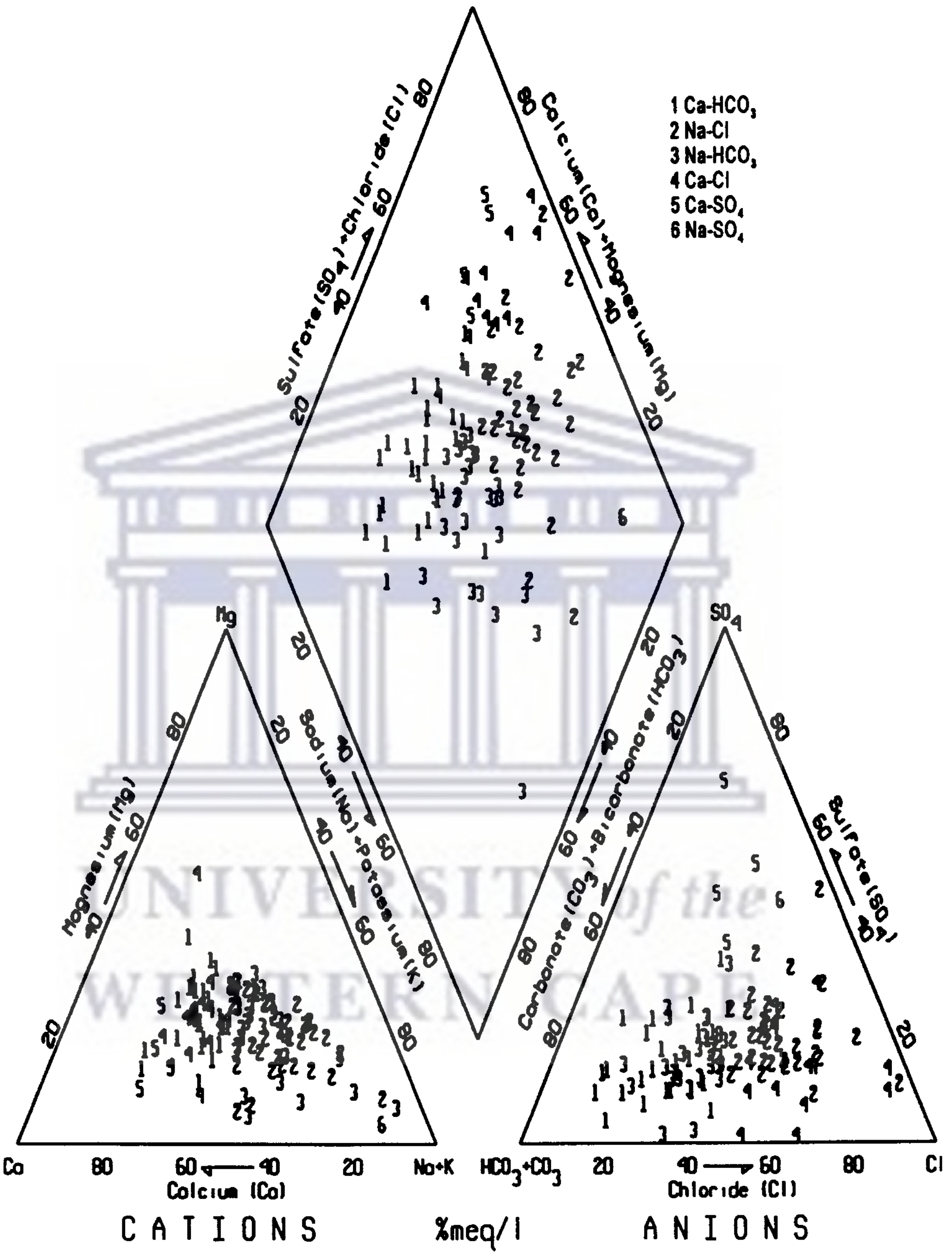


Figure 5.4. Piper diagram of all the groundwaters of the Sutherland area.

5.4.2.3 Distribution of the chemical constituents

The electrical conductivity (EC) map (Figure 5.5) is indicative of the influence that the local topography has on the groundwater composition. Groundwaters that occur in areas that are flat, areas that may act as sinks (i.e. rivers and valleys) are usually of a much poorer quality (> 200 mS/m) than the groundwaters occurring in areas that are sloping (i.e. hills and foothills) which tend to be fresher.

The groundwaters in the southern part of the study area were of the poorest quality and an increase in EC was observed towards the north. However, once the groundwater reaches a natural boundary (hills) the EC seems to decrease. The groundwaters drain towards the lower lying areas where it becomes static or stagnant with a concurrent increase in EC. Furthermore, the fact that most of the flatter lying areas and valleys have sufficient unconsolidated overburden, they are utilised for agricultural purposes with the subsequent effects of irrigation. This could cause a rise in the EC of such areas.

Sodium percentage maps have been applied (Tredoux and Kirchner, 1981) to indicate and interpret the direction in which discharge occurs. The percentages of sodium (Na%) of the total cations can indicate where recharge and discharge areas are situated. Areas where water tends to discharge will have a relatively higher Na% as opposed to areas where recharge occurs. The Na% map (Figure 5.6) validates the assumptions and indicate that lower lying areas (i.e. flat plains, valleys and rivers) acts as sinks to groundwater discharge. The sodium percentages of the groundwaters were much higher in the lower lying areas as opposed to the higher lying areas. In the northwestern part of the study area, boreholes sampled along the Renoster River show an increase in Na% down the flow path of the river. An indication that the groundwater behaves in a similar manner than that of the surface drainage.

The strontium (Sr), calcium (Ca), sulphate (SO_4) and chloride (Cl) maps (Figures 5.7-5.10) all show the same trends manifested by the EC map. These ions tend to increase in regions of discharge. The Ca map does not coincide with these trends for all the areas.

The potassium (K) map (Figure 5.11) does not show any correlation with topography. Potassium concentrations were not controlled by the salinity of the waters. Potassium is thus sourced from the geological material in the area. Anomalous potassium concentrations occur near Salpeterkop. High values to the southwest of Salpeterkop coincide with a fault zone with an adjacent K-trachyte dykelet, as mapped by De Wet (1975).

The nitrate (NO_3) map (Figure 5.12) shows the effects of land use practices. Isolated occurrences of high levels of nitrate are indicative of anthropogenic sources as no nitrogen containing geological material exists within the study area.

5.4.2.4 Groundwater evolution

The evolution of the groundwaters possibly follows the sequence in Table 5.4. There is also an increase in the mean TDS concentration in the evolution sequence. From table 5.4 an assumption can be made that boreholes with a facies 1 type water would occur in recharge areas or are more recent waters, whereas boreholes yielding a facies 6 type water would be water from discharge zones.

Talma (1981) found that water in Beaufort sediment, with a high salt content were relatively older than fresher waters. Groundwater that is dominated by HCO_3 (among the anions) is an indication of much younger waters with relatively short flow paths (Sowayan and Allayla, 1989).

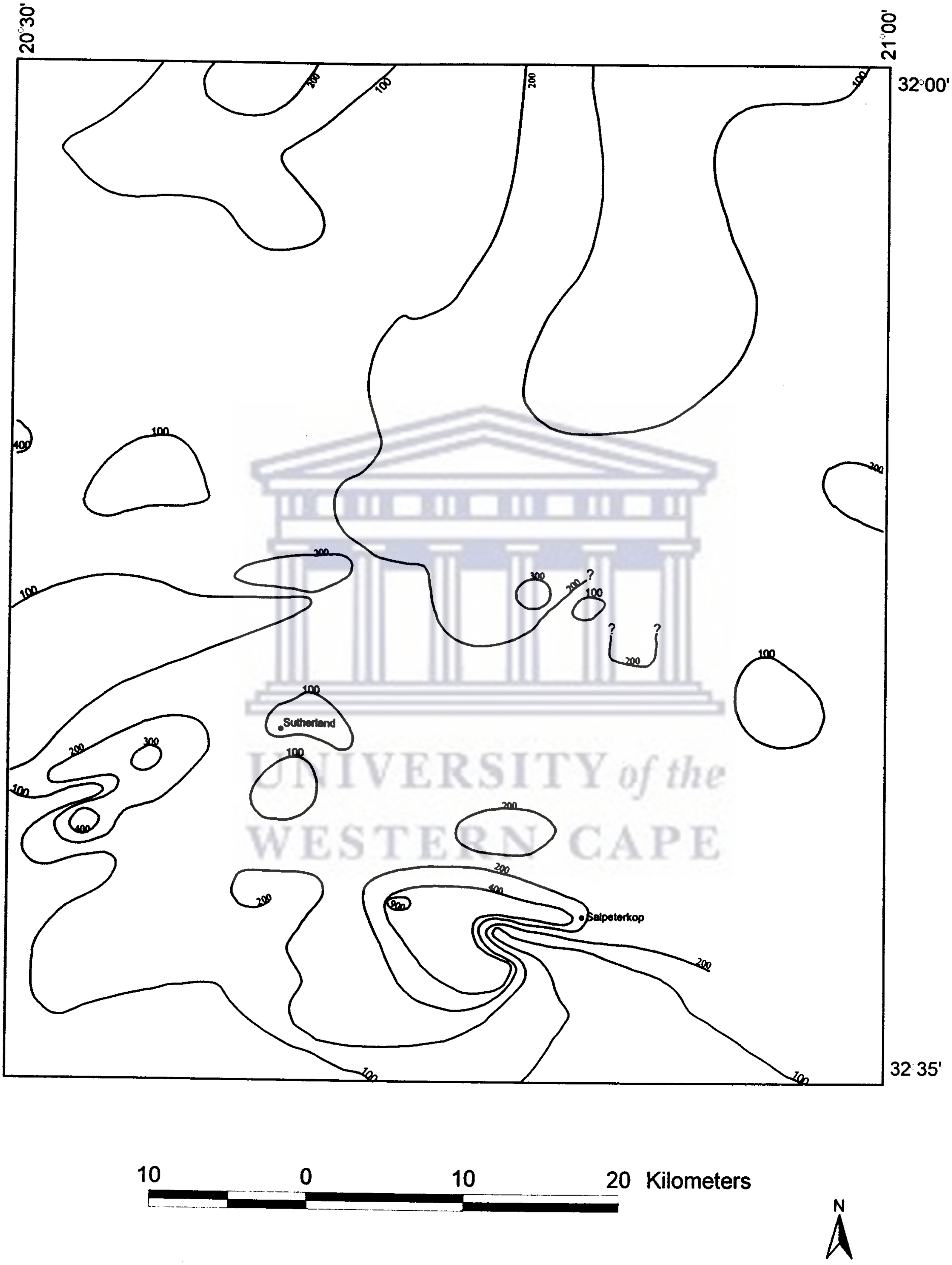


Figure 5.5. Electrical conductivity map for the study area

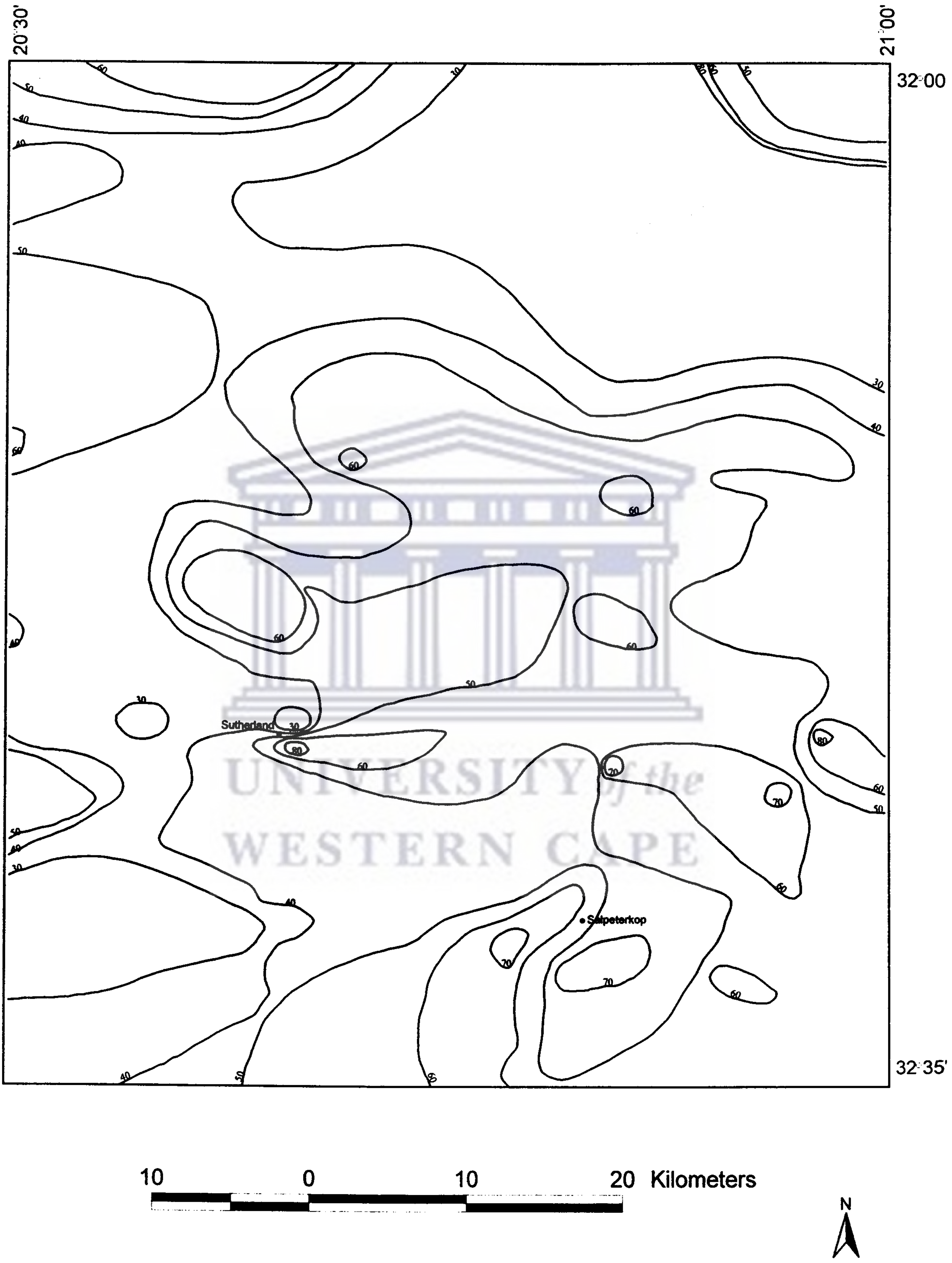


Figure 5.6. Sodium percentage map for the study area.

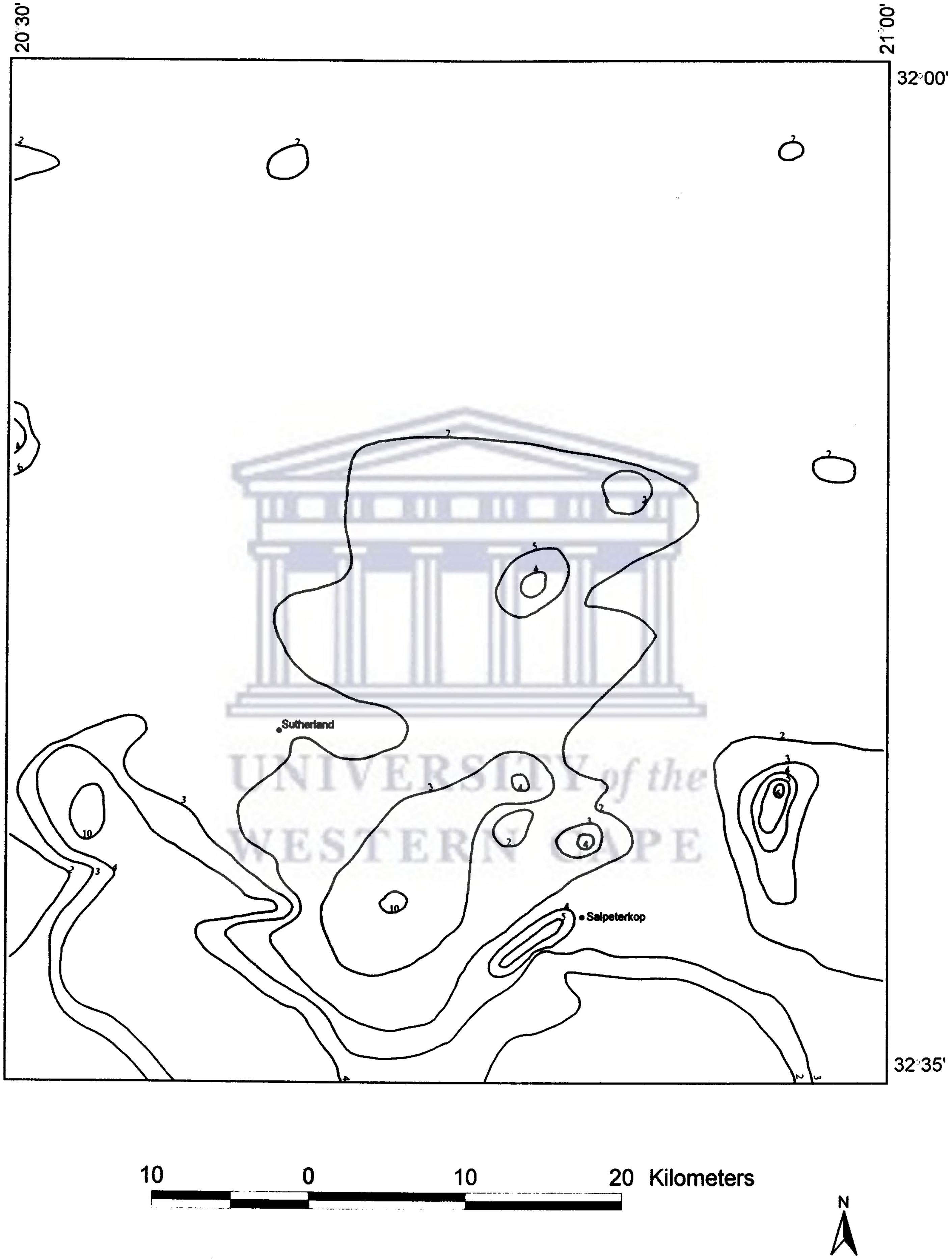


Figure 5.7. Strontium map for the study area.

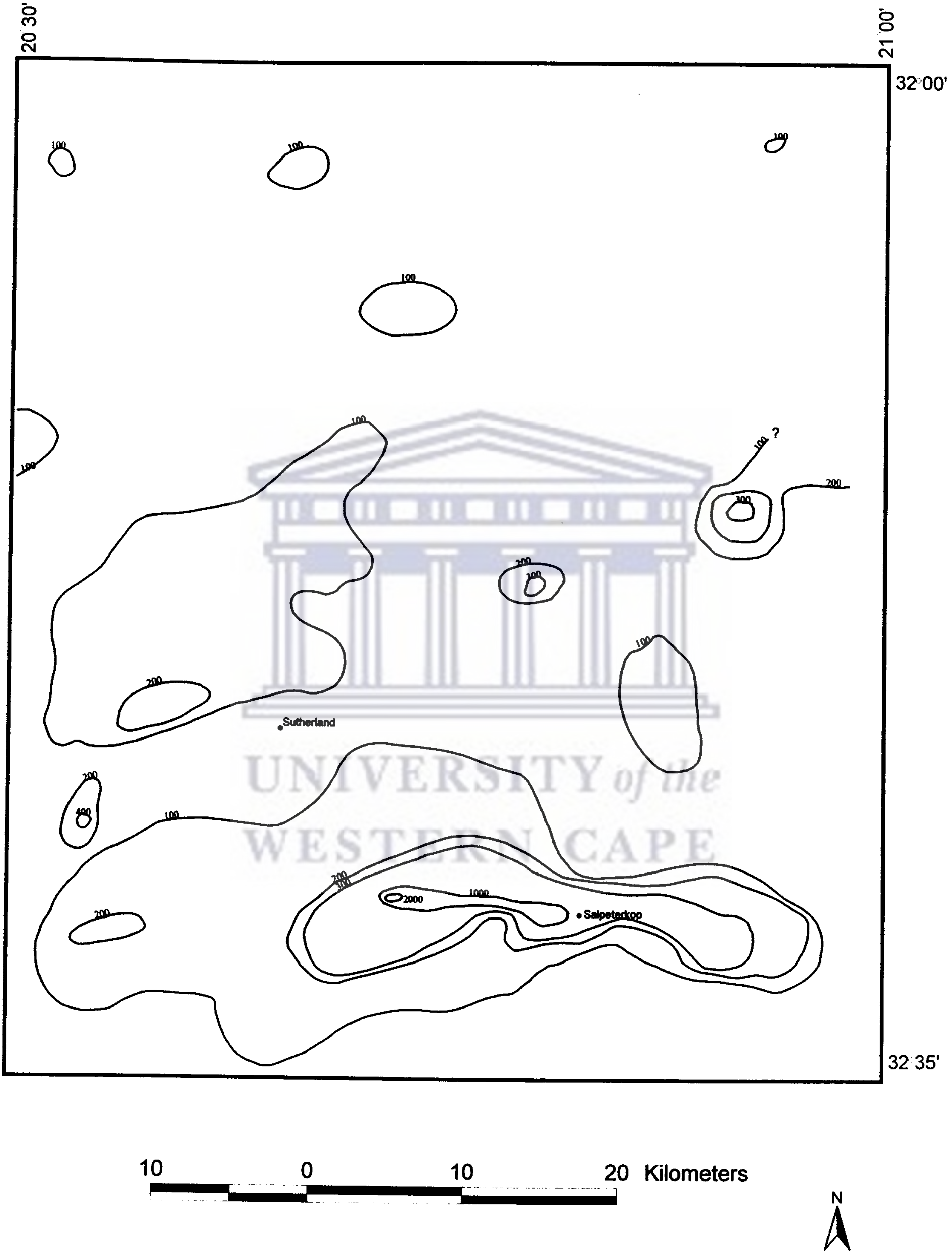


Figure 5.8. Calcium map for the study area.

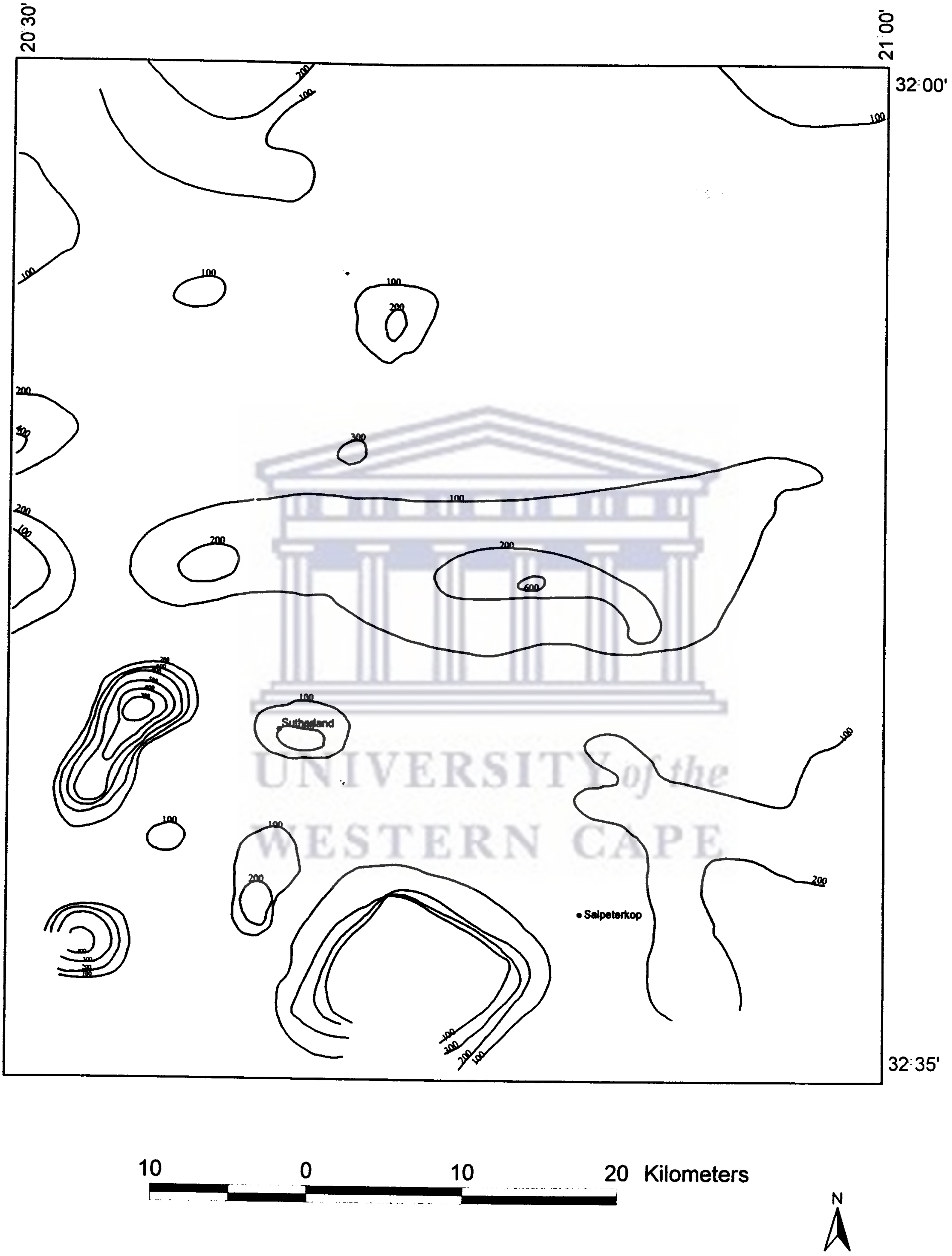


Figure 5.9. Sulphate map for the study area.

Figure 5.10. Chloride map for the study area.

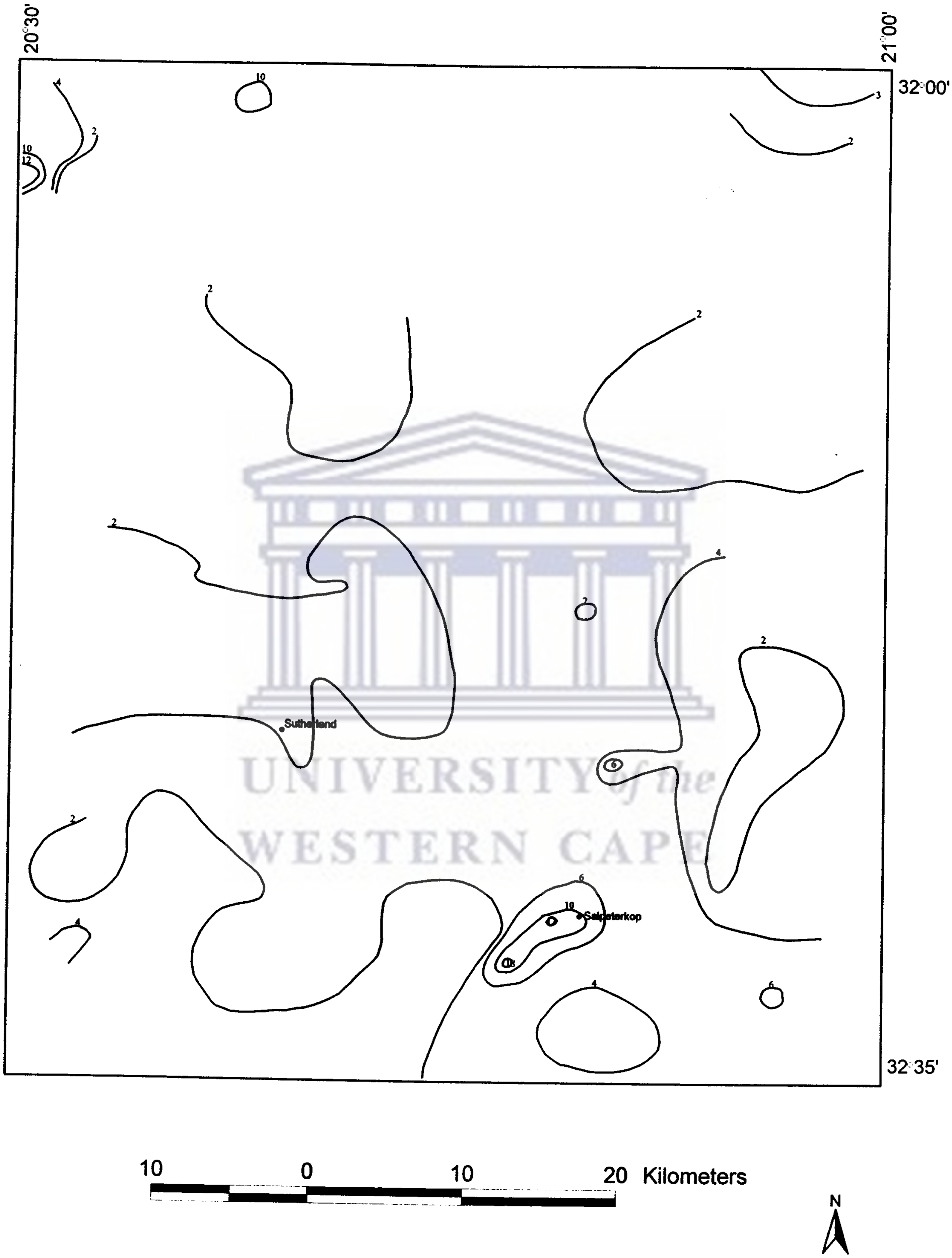


Figure 5.11. Potassium map for the study

Figure 5.12. Nitrate map for the study area.

Table 5.4. Hydrochemical facies and regimes of the groundwater.

Facies	Water type	Regime	Mean TDS (mg/l)
1	Ca-HCO_3	Recharge + static and discordinate	607
2	Na-HCO_3	Static + dynamic and coordinated	828
3	Ca-SO_4	Static and discordinate	825
4	Na-SO_4	Stagnant water	912
5	Ca-Cl	Static and discordinate + Ca-SO_4	1176
6	Na-Cl	Static discordinate + Ca-SO_4	1367

The development of the groundwater types in the study area can occur simultaneously within the fractured aquifer. If the water types are plotted for each borehole, Figure 5.13, no definite trend can be identified in terms of distribution of the groundwater types for the entire study area.

No regional patterns could be identified and large variations in salinity are observed over short distances. The regional fractured aquifers are possibly made up of groundwater compartments. These compartments are a result of the geological structures present in the area. Changes in the chemistry of the groundwaters may indicate localised recharge and discharge along these structures. The differences in the groundwaters could be a result of the topography of the study area as well as the vertical heterogeneity in lithology from which the groundwater was extracted.

From the statistical, graphical and spatial analyses of the data set, certain key factors and processes were identified. The chemical character of the groundwater is predominantly controlled by the infiltration of evaporated surface and subsurface water, the topographical nature of the catchments, geological influences (i.e. the processes of dissolution, precipitation and ion exchange) and the effects of man. Using hydrochemical techniques, the effects of these factors would be ascertained.

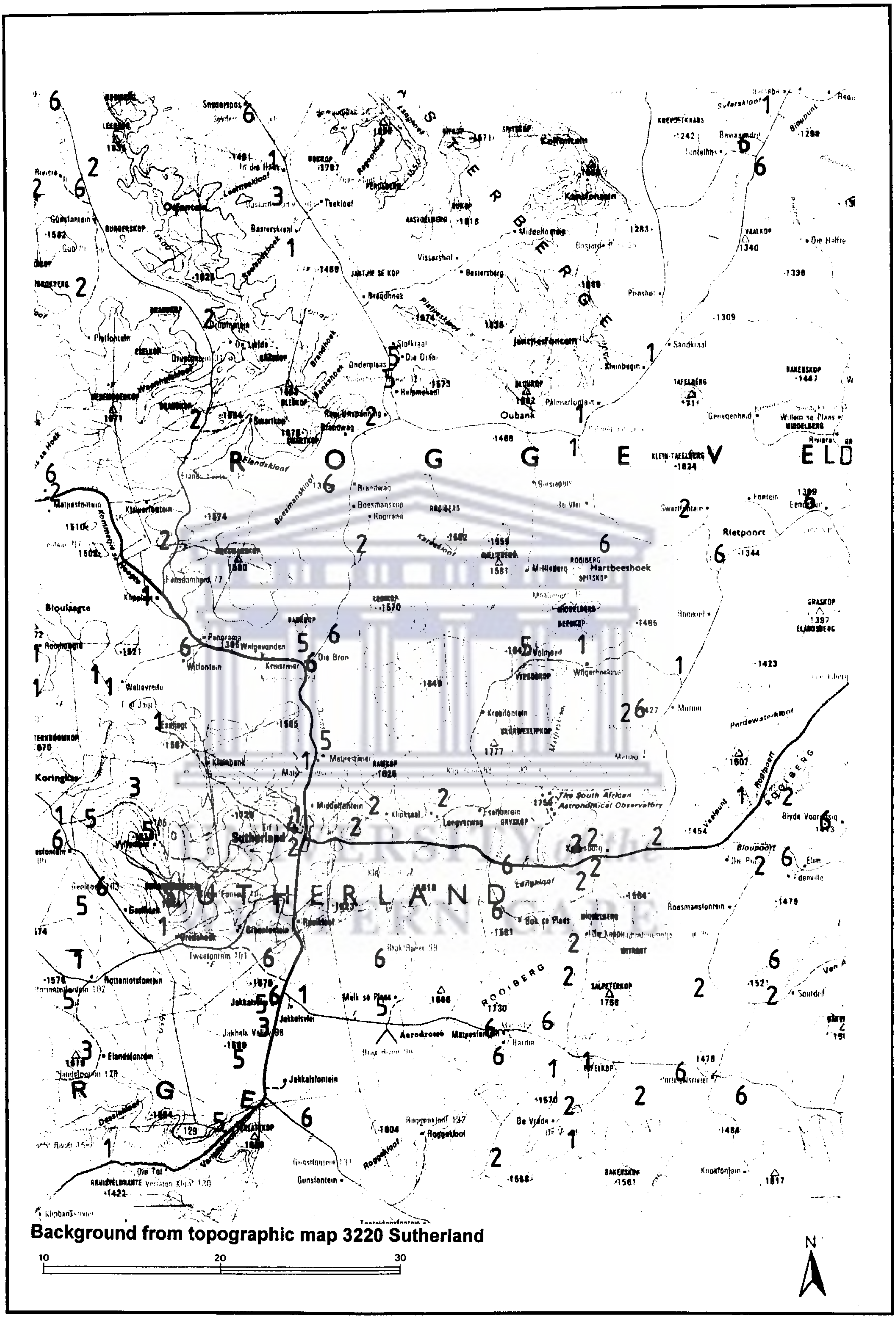
5.5 FACTORS AFFECTING GROUNDWATER CHEMISTRY

5.5.1 Influence of topography on the groundwater chemistry

In the data set for the whole area, a relationship exists between the topography and the salinity of the groundwater. This relationship exists due to the fact that flat areas are usually associated with areas of discharge with the water flow becoming more sluggish or static and evapotranspiration is more pronounced. In higher lying regions, the residence time of the water is low and the water tends to flow away from these regions due to the hydraulic gradients that exists. The effect of evapotranspiration is thus less pronounced. The most abundant water type of the area (i.e. Na-Cl water) is predominantly found in flatter areas while in the higher lying areas, a more Ca/Na-HCO_3 water type dominates.

The topography has a definite influence on the water chemistry. From Figure 5.14 it is evident that certain points with low Cl and TDS values, located on hills or higher lying areas, plot in the lower left-hand corner of the diagram. Groundwater from flat areas plots more towards the right-hand corner of the diagram, showing an increase in the Cl content of the water and the subsequent increase in the TDS. Intermediate areas plot between the high and flat lying areas. Sampling points located on flat areas also plot at points of higher lying areas, indicating that the topography does not absolutely determine its chemical composition. These phenomena must be due to factors other than residence times and evapotranspiration.

Topography determines the direction in which groundwater and surface water flow. Groundwater flow will occur along joint and fracture zones, caused by dolerite intrusions, which is prevalent in the area. The various sills and dykes may form impermeable barriers to groundwater flow. They can also cause permeable zones, causing mixing between two compartments. The orientation of these structures would ideally control the local flow regimes. The mean TDS increases from areas of higher topographical settings to more flat topographical settings as depicted in Table 5.5.



1 = Ca-HCO_3 2 = Na-HCO_3 3 = Ca-SO_4 4 = Na-SO_4 5 = Ca-Cl 6 = Na-Cl

Figure 5.13. An areal plot of the groundwater types of each borehole.

Table 5.5. Average groundwater chemistry for various topographical settings.

	EC (mS/m)	pH	Cl	Na	Ca	HCO_3
Hills	77.58	7.17	49.5	35.28	54.9	230.7
Slopes	90.68	7.38	125.3	114.5	72.6	310.8
Foothills	130.6	7.40	203.3	118.7	94.6	324.1
Rivers	137.8	7.39	206.3	147.5	97.1	332.2
Valleys	166.5	7.21	221	150.1	96.9	342.4
Flats	208.1	7.29	412.4	210.4	139	324

All values in mg/l unless otherwise indicated

The Ca and HCO_3 values in the higher lying areas are much lower than in the lower lying areas. This would suggest that direct recharge and the subsequent dissolution of carbonate minerals not only occur but is limited to the higher lying areas. Recharge at fracture zones would be favoured. The Na and Cl content of the groundwaters increase from higher lying areas to lower lying areas. The groundwater is generally fresher, at topographical higher lying areas, where it is not subjected to concentration as in the lower lying areas.

The local topography would also determine the location and amount of salt accumulation because of evaporation. Areas that act as sinks, usually flatter areas, and localised depressions are ideal localities for the ponding of water. Topography and its relation to drainage are the major factor that influences the accumulation of salts.

5.5.2 Influence of evapotranspiration on the groundwater chemistry

The annual mean precipitation in the study area is less then 300 mm/year. The rate of annual potential evapotranspiration is 5-6 times more than the mean annual precipitation. These phenomena have a marked effect on the groundwater composition.

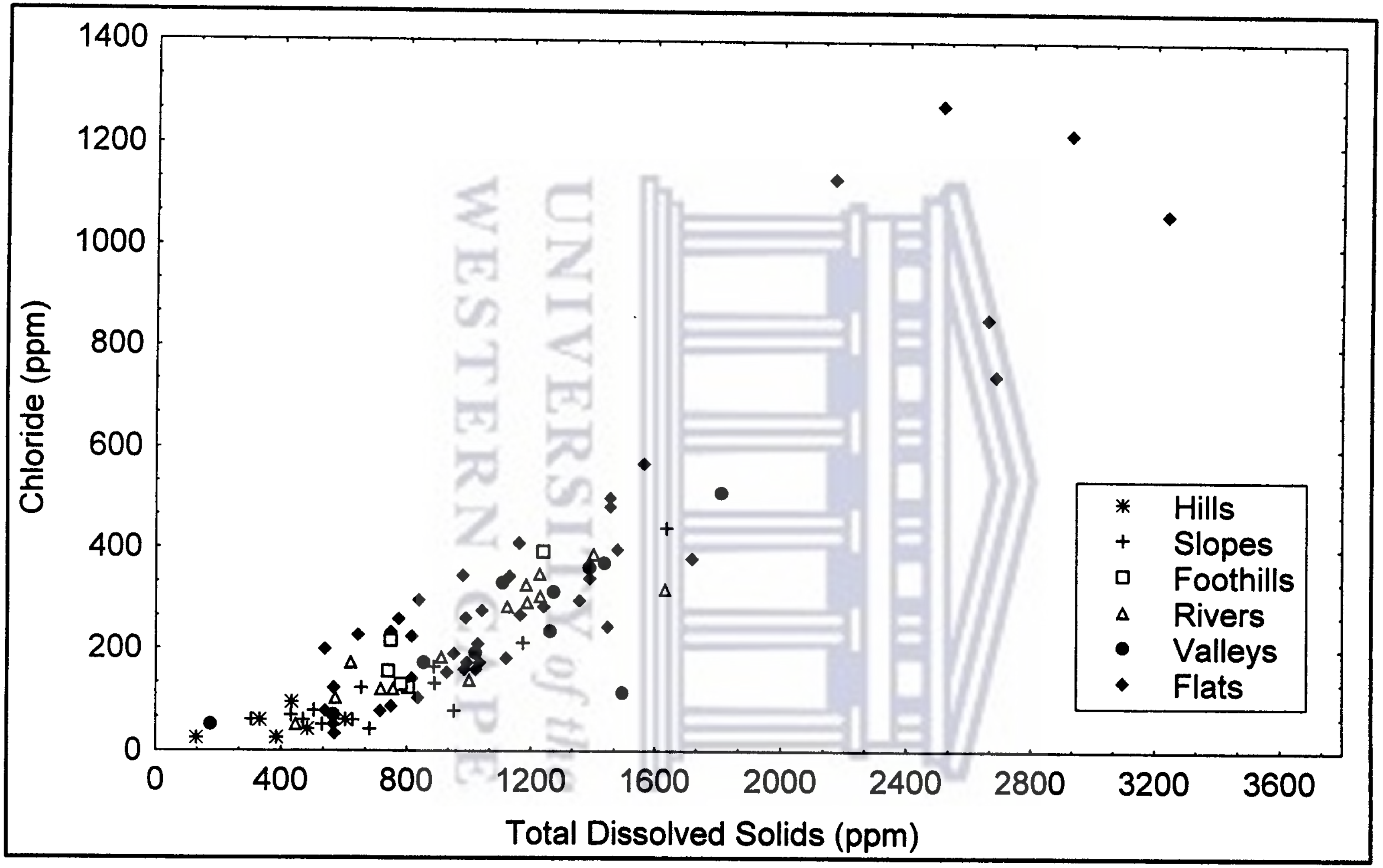


Figure 5.14. Relationship between Cl and TDS and its relation to the topography.

Surface water would generally flow from higher lying areas to become static in flat areas or local depressions. In these depressions ponding of the water occurs. The water is evaporated and salts accumulate at the surface. During the next rain event the salts are dissolved and transported to the subsurface (i.e. the unsaturated and saturated zones) with the cycle repeating itself. High salinity water is in this way recharged and therefore high TDS waters are found in flatter areas.

The phenomenon of high salinity water in flatter areas is proven by the behaviour of the isotopes $\delta^{18}O$ and $\delta^{2}H$. When water evaporates either from surface water bodies or saturated soils, there is an enrichment of both $\delta^{18}O$ and $\delta\ ^{2}H$ in the residual liquid. Isotopes with smaller atomic mass (^{1}H and ^{16}O) are preferentially transformed into the gas phase. Evaporated water can then be distinguished by its relative enrichment of $\delta^{18}O$ and its deviation from the GMWL (Figure 5.15). The sampling points seem to plot away from each other and not in a cluster. The importance of this phenomenon is the fact that the groundwater is not uniform. It does not have the same origin. A common recharge source is not likely due to the variability of $\delta^{18}O$ in terms of locality.

Three points plot to the left of the GMWL and may suggest processes other than evaporation. The local rainwater line are usually located above the GMWL. The isotopic enrichment of $\delta^{18}O$ and $\delta^{2}H$ in Figure 5.15 suggest that the main cause of the groundwater salinity is the percolation of evaporated water to the subsurface. This shows that the recharge is very slow and that it is derived from ponded water. Furthermore, recharge occurs only during excessive rainfall events. Evaporated water infiltrates into the subsurface through preferential pathways. The points on or very near to the GMWL indicate that the water did not evaporate before infiltration (i.e. infiltration was rapid).

No correlation exists between the Cl concentrations and the $\delta^{18}O$ plot (Figure 5.16) and would thus indicate that no relationship exists between isotopic enrichment and groundwater salinity as a result of the effects of evaporation. The differences in $\delta^{18}O$ and Cl are an indication that the waters may be unrelated and that different infiltration conditions occur. It is likely that this relationship could have been lost due to the effect of mixing of different water bodies. The effect of mixing and the existence of different water bodies, could be seen from a borehole (HEB6) pumped for four hours, with isotope sampling at 1 min after pumping started and after 4 hours of pumping.

In a plot of altitude against the $\delta^{18}O$ content of the specific boreholes (Figure 5.17), a trend emerges. Water originating from precipitation on higher elevations is considerably depleted in the stable isotope ($\delta^{18}O$) relative to water originating from lower altitudes. Depletion of the heavier stable isotopes occurs as water vapour condenses in an air mass which is forced upwards by changes in the topography (Mook, 1994). Stable isotope concentrations in intense rainfall and rainfall occurring at higher altitudes are lighter. Several water points plots away from the regression line indicating that they are not controlled by the same processes and may be the result of seasonality and the effect of temperature.

5.5.3 Influence of geology on the groundwater chemistry.

5.5.3.1 Introduction

The geological materials that constitute the crust of the earth are the primary reservoir and ultimate source of most major elements and trace elements in soils and in natural waters (Bricker and Jones, 1995). Dissolution, precipitation and cation exchange of constituents in groundwater are the main factors responsible for the variability of the chemical quality of groundwater. On encountering soil and rock, water incorporates major and trace elements by decomposing and dissolving rock minerals.

The geology of the area, as described in Chapter 3, is made up of predominantly sandstones, mudstone and dolerites, with minor occurrences of shales, carbonatites and melilite basalts. The lithological units are near horizontal and changes in the lithology are frequent. The geological information is very limited, especially information on vertical profiles of sampled boreholes.

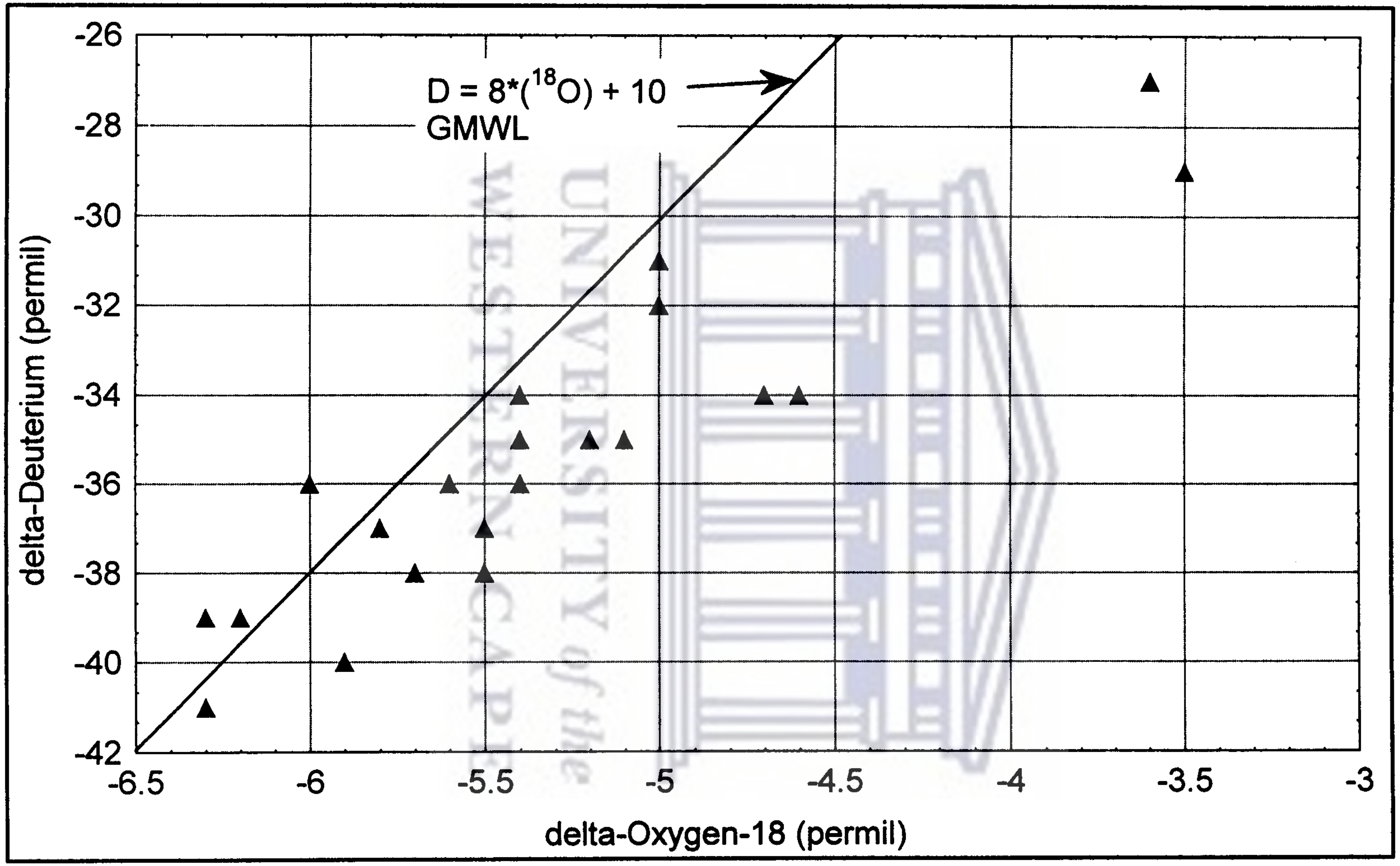


Figure 5.15. Deuterium versus Oxygen-18 for selected wells.

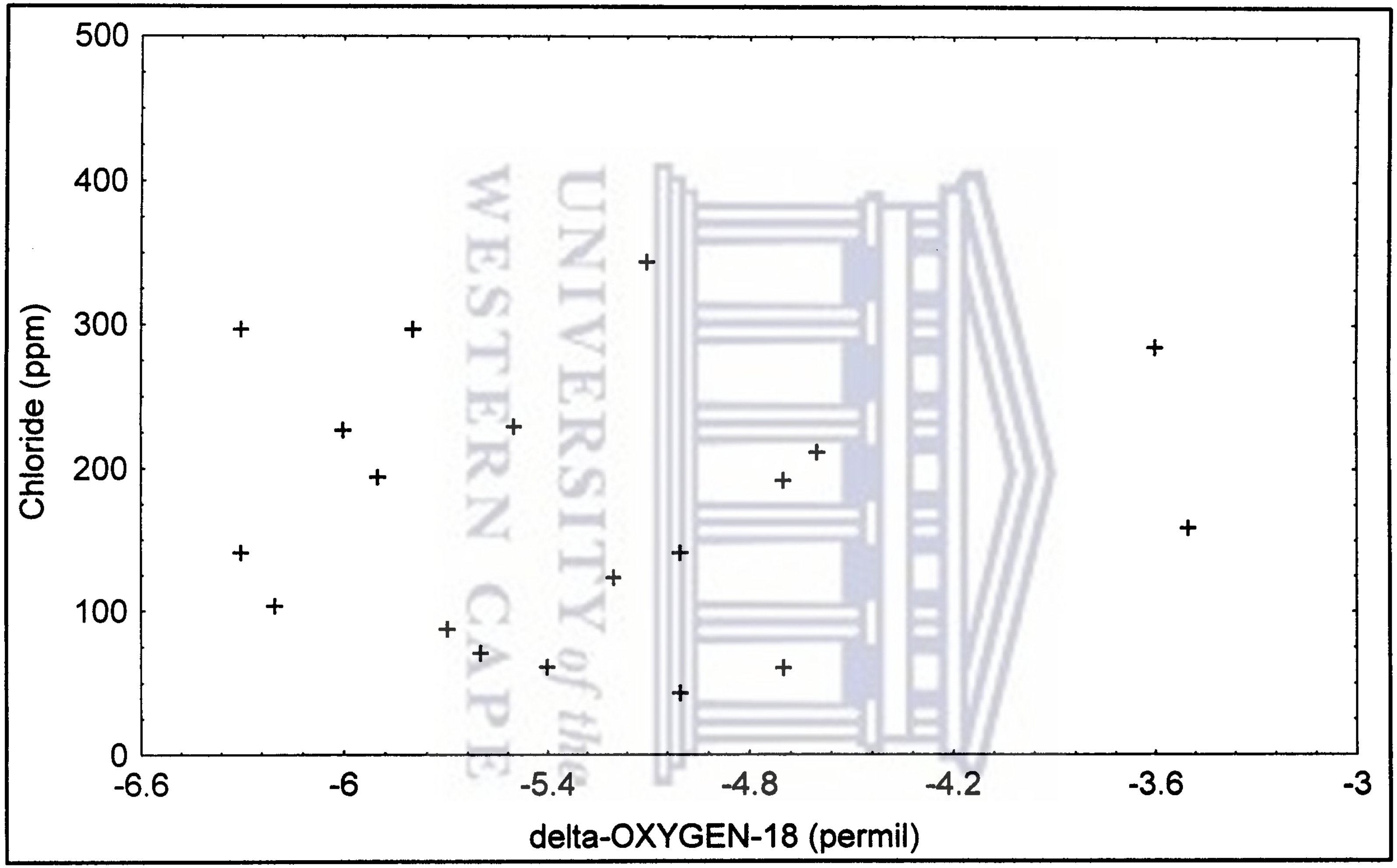


Figure 5.16. Plot of Cl versus oxygen-18 for selected wells.

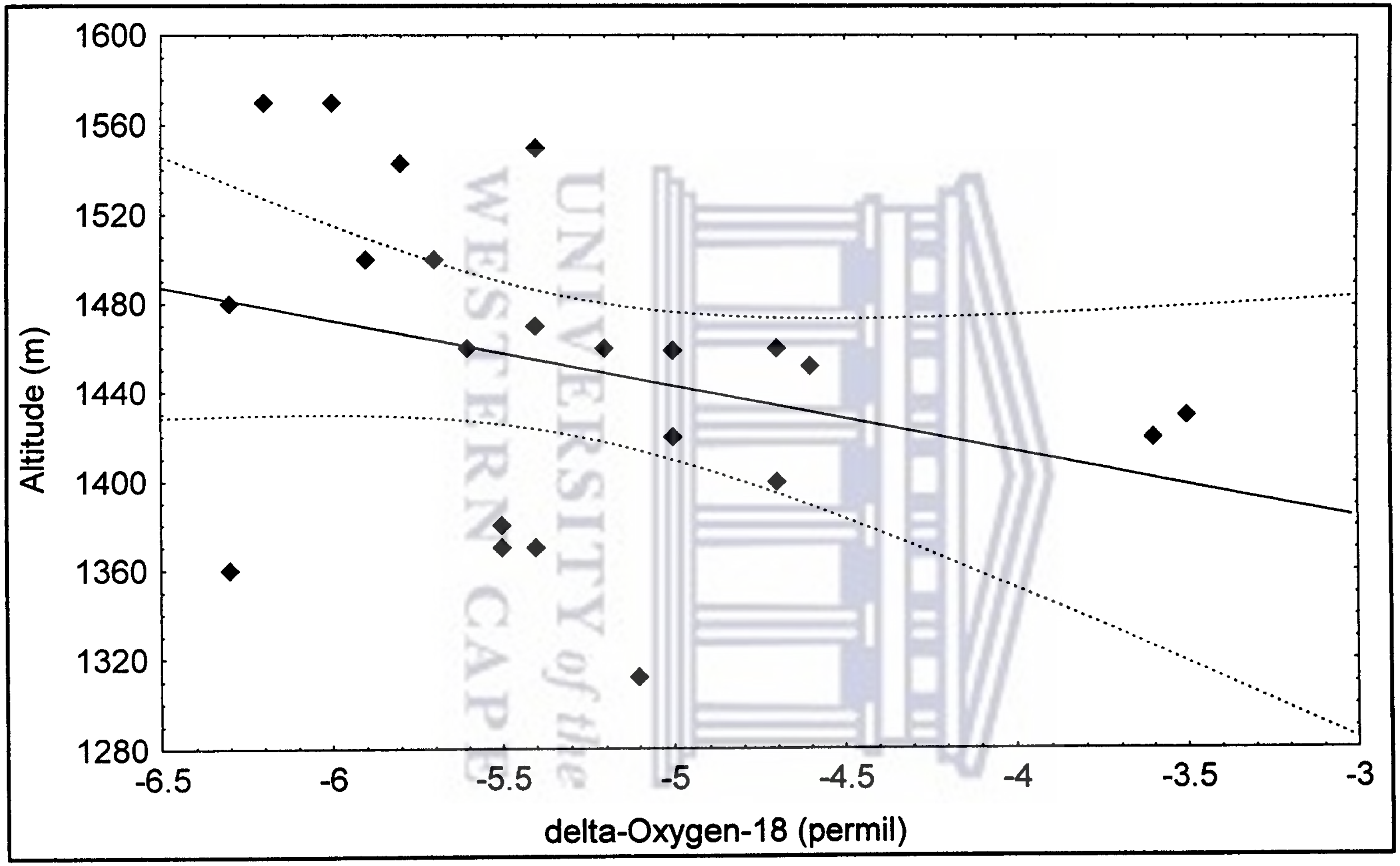


Figure 5.17. Plot of altitude versus $\delta^{18}O$ for selected wells.

5.5.3.2 Mineralogy

The changes in lithology can exert a significant influence on the water chemistry. Freeze and Cherry (1979) postulated a theory on the order in which groundwaters encounter strata of different mineralogical composition which can exert an important control on the final water chemistry. Different lithological units can influence the chemistry of groundwater due to different thermodynamic constraints (Freeze and Cherry, 1979). Table 5.6 gives an approximate composition of the dominant rocktypes found in the area.

Table 5.6. Approximate mineralogical composition of the major rocktypes as found in the area (Bricker and Jones, 1995; De Wet, 1975).

Rocktype	**Mineralogy**	**Mineral Composition**	**Trace element contents**[1]
Sandstone	Quartz	SiO_2	
	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	F, Ca, Na, Ba, Mn
	Feldspars	$K,Na(AlSi_3O_8)$ and $Ca,Ba(Al_2Si_2O_8)$	
	Plagioclase	$(Na,Ca)Al(Al,Si)Si_2O_8$	K, Sr, Ba, Mn
	Chlorite	$(Mg,Fe)_5(Al,Fe)_2Si_3O_{10}(OH)_8$	
	Muscovite	$KAl_3Si_3O_{10}(OH)_2$	
	Calcite	$CaCO_3$	Sr, Ba
	Orthoclase	$K_2O.Al_2O_3.6SiO_2$	
	Illite matrix	$K_{0.7}{}^{xii}[Si_{3.3}Al_{0.7}]^{iv}[Al_2]^{vi}O_{10}(OH)_2$	
Mudstone	Quartz	SiO_2	
	Calcite	$CaCO_3$	Sr, Ba
	Chlorite	$(Mg,Fe)_5(Al,Fe)_2Si_3O_{10}(OH)_8$	
Shale	Quartz	SiO_2	
	Illite	$K_{0.7}{}^{xii}[Si_{3.3}Al_{0.7}]^{iv}[Al_2]^{vi}O_{10}(OH)_2$	B
Dolerite	Quartz	SiO_2	
	Pyroxene	$(Na, Ca,Mg)SiO_3$	Al, Na, Mn, K, Ni, Sr
	Magnetite	Fe_3O_4	Al, Mg, Mn, Zn,Cu
	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	F, Ca, Na, Ba, Mn
	Plagioclase	$(Na,Ca)Al(Al,Si)Si_2O_8$	
	Olivine	$2(Mg,Fe)O.SiO_2$	
	Ilmenite	$FeO.TiO_2$	
Carbonatite Intrusive	Pyrite	FeS_2	
	Ilmenite	$FeO.TiO_2$	
	K-feldspar	$K,Na(AlSi_3O_8)$	Na, Ca, Ba, Sr
	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	F, Ca, Na, Ba, Mn
	Barite	$BaSO_4$	Ba, Sr
	Calcite	$CaCO_3$	Sr, Ba

[1] Only trace element contents are indicated that are used in this study.

Trace element compositions of the various rocktypes are available from three borehole logs in both published and unpublished material (Chevallier (pers. comm.); Geological Survey, 1983). Hem (1989) compiled a list of elements illustrating the estimates of the crustal abundance of 93 elements for both igneous and sedimentary rocks. The estimates are combined with the available average trace element composition of the three borehole logs in Table 5.7.

The uncertainties of the values given by Hem (1989) are high (Bricker and Jones, 1995). However, the estimates give a general indication of the element distribution among the major rocktypes.

Table 5.7. **Average element composition, in ppm, of sandstones, mudstones, shales, dolerites and carbonatites (Chevallier (pers. comm; Geological Survey, 1983 and Hem, 1989).**

Element	Sandstone	Mudstone	Dolerite	Carbonatite	Mean groundwater composition[4]
Ca[1]	22 400		36 200[5]		107
Na[1]	3870		28 100[5]		159
Cl[1]	15		305[5]		269
K[1]	13 200		25 700[5]		3
Mg[1]	8100		17 600[5]		40
Ba[2]	435	624	190	4756[3]	0.1
Mn[2]	50	62	120		0.1
Sr[2]	217	263	190	1144[3]	3
P[2]	57	60			0.1
Ni[2]	9	19	54	91[3]	0.01
Cu[2]	13	37	93	27[3]	0.01
Zn[2]	59	86	109	171[3]	0.1

[1]Hem (1989); [2]Geological Survey (1983) and [3]Chevallier (pers. comm.). [4]This study. [5]Values for igneous rocks.

The oxide and trace silicate minerals, as well as quartz minerals, do not have a significant effect on the groundwater. These minerals are normally unreactive or react very slowly under the groundwater temperature and pH conditions. The faster reacting minerals in an aquifer usually determine or dominate the groundwater chemistry (Katz and Choquette, 1991).

The contribution of each mineral to the groundwater chemistry is a complex and often erroneous task to quantify. The use of mass balance equations and modelling techniques are often difficult to compute due to a lack of information and the influence the background chemistry may exert on the water chemistry.

The use of relationships between ionic species may indicate the elements contributing to the groundwater chemistry due to various hydrochemical processes at increasing salinities. The chloride ion is a useful conservative ion that could be used to determine the effects of concentration, and in the area, it is an excellent indicator of increasing salinity. This is proved by the statistical analyses. If an element is added to the groundwater as a result of mineral weathering, then it would not show any correlation with Cl. Ionic species in the data set that does not show any relationship with Cl are (Table 5.2): barium, potassium, manganese, fluorite and boron. These elements are thus unaffected by salinisation of the groundwater. At increasing salinities, the relative contribution of mineral weathering decreases due to the increasing action of cation exchange.

The sources of barium in the geological material could be barite minerals (associated with the Salpeterkop Intrusive Complex), feldspars (e.g. celsian $Ba[Al_2Si_2O_8]$) and biotite. Potassium may be sourced from the minerals biotite, k-feldspars, plagioclase, muscovite and orthoclase. Manganese may be derived from the minerals rhodochrosite, pyroxenes, biotite, magnetite and olivine. Apatite and fluorite may be the main source minerals for the fluoride ions in the groundwaters of the area.

Elevated levels of the trace elements at any particular site would indicate the influence of a particular rocktype on the groundwater chemistry. These elevated levels can then be used to define the type of rock that is prominent at any specific site. Barium and strontium levels would thus be elevated in areas underlain by the carbonatite and associated rocks. Manganese would be elevated in areas of doleritic rocks. However, the manifestation of the influence of the geology is lost by the effect of groundwater concentration as a result of evaporation.

In order to relate the influence of the geology on the groundwater composition, one would have to look at the geohydrochemical processes that occur between the geological environment and the groundwater.

5.5.3.3 Dissolution

Initial precipitation charged with CO_2 forms a mild acid, carbonic acid (H_2CO_3). Groundwaters in the area became charged with CO_2 during the infiltration of precipitation. This is proven by the fact that the partial pressure of CO_2 (pCO_2) in the groundwaters is higher than the pCO_2 of the earth's atmosphere (i.e.0.0003 atm) (Freeze and Cherry, 1979). The average pCO_2 in the Sutherland groundwater is 0.02 atm. The higher concentrations are the result of root respiration and the decomposition of organic matter (Schot and Wassen, 1993).

The pCO_2 of the groundwaters was calculated using the NETPATH (Plummer et al., 1992) computer program through a WATEQF subroutine. The higher concentrations of Ca, Mg, Na and K in the groundwaters relative to the precipitation chemistry are indicative of the weathering of minerals containing these cations (Katz, 1989).

Carbonate dissolution seems to be a common occurrence in the study area, specifically calcite dissolution, and would be used to explain the process of dissolution. In areas of recharge, Ca-HCO_3 type waters dominate on the assumption of the following simplified reaction:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3$$

Calcium is liberated from the carbonate minerals commonly occurring within the rock matrix of the aquifer materials. Calcite is the most favoured carbonate mineral present in the aquifer as it is readily available in the rock matrices of the sandstones and mudrocks of the area. Calcite is the favoured carbonate mineral above Mg-carbonates (dolomite) due to the fact that the Ca/Mg ratio for the groundwaters is much larger than unity. This is due to the low amounts of Mg found in the groundwaters relative to the Ca ions.

5.5.3.4 Precipitation and saturation states

Saturation indices (SI) were calculated with the NETPATH (Plummer et al., 1992) computer program, through a WATEQF subroutine. Limits set for the results given in Appendix IV, ranges between -1 for the lower limit for all undersaturated waters and +1 for oversaturated waters. The log scale is used to adapt large deviations from equilibrium. Undersaturation (SI <-0.1) would result in the dissolution of a specific mineral while oversaturation (SI >0.1) results in the precipitation of minerals. The reason for not taking 0 as equilibrium in this study is due to the uncertainties in the measurements of pH. An error of ±0.05 pH units leads to an uncertainty of ±0.05 units in the SI of minerals and in view of uncertainties in Ca^{2+}, Mg^{2+} and HCO_3^- analyses, the total uncertainties are in the order of ±0.1 units of SI (Langmuir, 1971). Thus, equilibrium would be around -0.1 and 0.1 to compensate for any analytical uncertainties.

The use of activity-activity diagrams indicates the saturation state of the groundwater with respect to various mineral phases. Saturation indices are useful in determining the saturation state of any ion in a water sample.

Activity-activity diagrams have been prepared for the minerals calcite, gypsum, strontianite, barite, and fluorite (Figures 5.18 – 5.22). The log activities of the various ions are also given in Appendix IV. The saturation lines in the figures were derived from the solubility products of the various mineral phases. All points that plot below the saturation line indicate that the groundwater is undersaturated with respect to the specific mineral and all points plotting above the line, indicate oversaturation. Points plotting on and near the saturation line, indicate that the groundwaters are saturated with respect to the mineral phase. The solubility products of the various mineral phases are outlined in Table 5.8.

Table 5.8. Solubility products of the minerals (Appelo and Postma, 1994).

Mineral	Reaction	Solubility Product
Calcite	$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^-$	$10^{-8.48}$
Strontianite	$SrCO_3 \leftrightarrow Sr^{2+} + CO_3^-$	$10^{-9.271}$
Fluorite	$CaF_2 \leftrightarrow Ca^{2+} + 2F^-$	$10^{-10.6}$
Gypsum	$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^-$	$10^{-4.58}$
Barite	$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^-$	$10^{-9.97}$

The groundwaters in the Sutherland region are saturated to oversaturated with calcite and undersaturated with respect to the minerals gypsum, strontianite and fluorite (Figures 5.18, 5.19, 5.20, 5.22). All points lie around the saturation line for barite (figure 5.21) with approximately equal distribution between undersaturation and oversaturation.

Calcium concentrations in the groundwaters are controlled by calcite saturation. The Ca ions are consumed by calcite saturation. Gypsum dissolution (i.e. increasing the Ca concentrations in solution) causes calcite precipitation (Appelo and Postma, 1994). Cation exchange may also be a major process for the removal and addition of Ca in solution. Gypsum is undersaturated because it is highly soluble and due to the fact that it is a major source of Ca for calcite saturation.

Gypsum is a major source of SO_4 in the groundwaters of the area. The SO_4 is then in turn reduced to H_2S, responsible for the "rotten egg" odour of the groundwaters in the area. The undersaturation of gypsum ($CaSO_4$) may be a result of the loss of Ca ions due to the effect of cation exchange and due to the common ion effect, whereby barium is the preferred ion to attach itself to SO_4, forming barite. Barium concentrations are controlled by barite ($BaSO_4$) equilibrium. Barite could also be less soluble then gypsum. Barite crystals have also been observed in the joints of the Beaufort sandstones (De Wet, 1975).

Calcite precipitation also causes a decrease in CO_3, which in turn causes the dissolution of other carbonate minerals (i.e. strontianite). This is probably the cause of the undersaturation of strontianite in the Sutherland groundwaters. Cation exchange processes could also be responsible for strontianite undersaturation. Fluorite saturation is not achieved in the groundwaters of the Sutherland area. The fluorite dissolution may be caused by the effect of complexing, which has the effect of reducing free Ca and fluorite activities (Nordstrom and Jenne, 1977). Fluorite dissolution would be achieved under these conditions. Undersaturation of most of the mineral phases may be due to the loss of ions as a result of cation exchange.

5.5.3.5 Cation exchange

The groundwater in the study area evolves from a Ca-HCO_3 type water towards a Na-Cl type water. Several processes thus occur between the initial Ca-HCO_3 type water to a more Na-Cl type water that is presumably much older at the end of the groundwater evolution sequence.

Some ions would combine and precipitate as mineral phases when their saturation states are reached and other ions would enter into ion-exchange reactions (Sowayan and Allayla, 1989). The only ion that is not affected by these processes is chloride, because of its conservative nature.

The different groundwater types in the study area are not only indicative of the changes in the major anions in the groundwater, but also of the major cations in the groundwater samples. Na-HCO_3 is formed by the replacement of Ca with Na within a Ca-HCO_3 type water. Similar exchange reactions are possible for the formation of Na-SO_4 type waters from a Ca-SO_4 type water. These processes are indicative of a natural groundwater evolution sequence. At the end of the evolution sequence the Na-Cl type water is dominant. The occurrence of Ca-Cl type waters is indicative of the refreshening of saline waters (usually Na-Cl type waters) with the replacement of Na by Ca due to the reversal of the ion exchange processes. Refreshening may occur as a result of mixing with a fresher Ca-type recharging water.

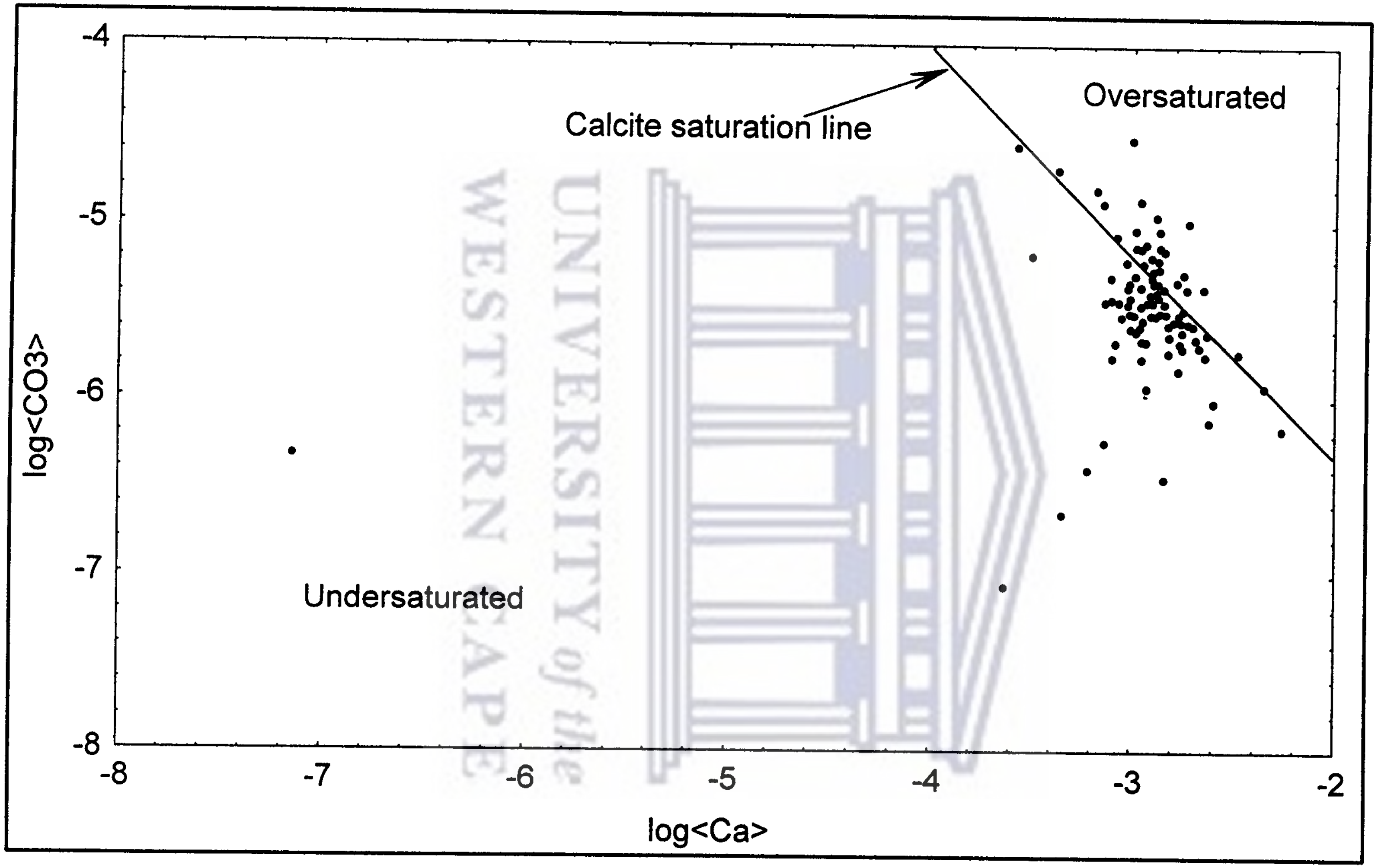


Figure 5.18. Activity-Activity diagram for calcite saturation.

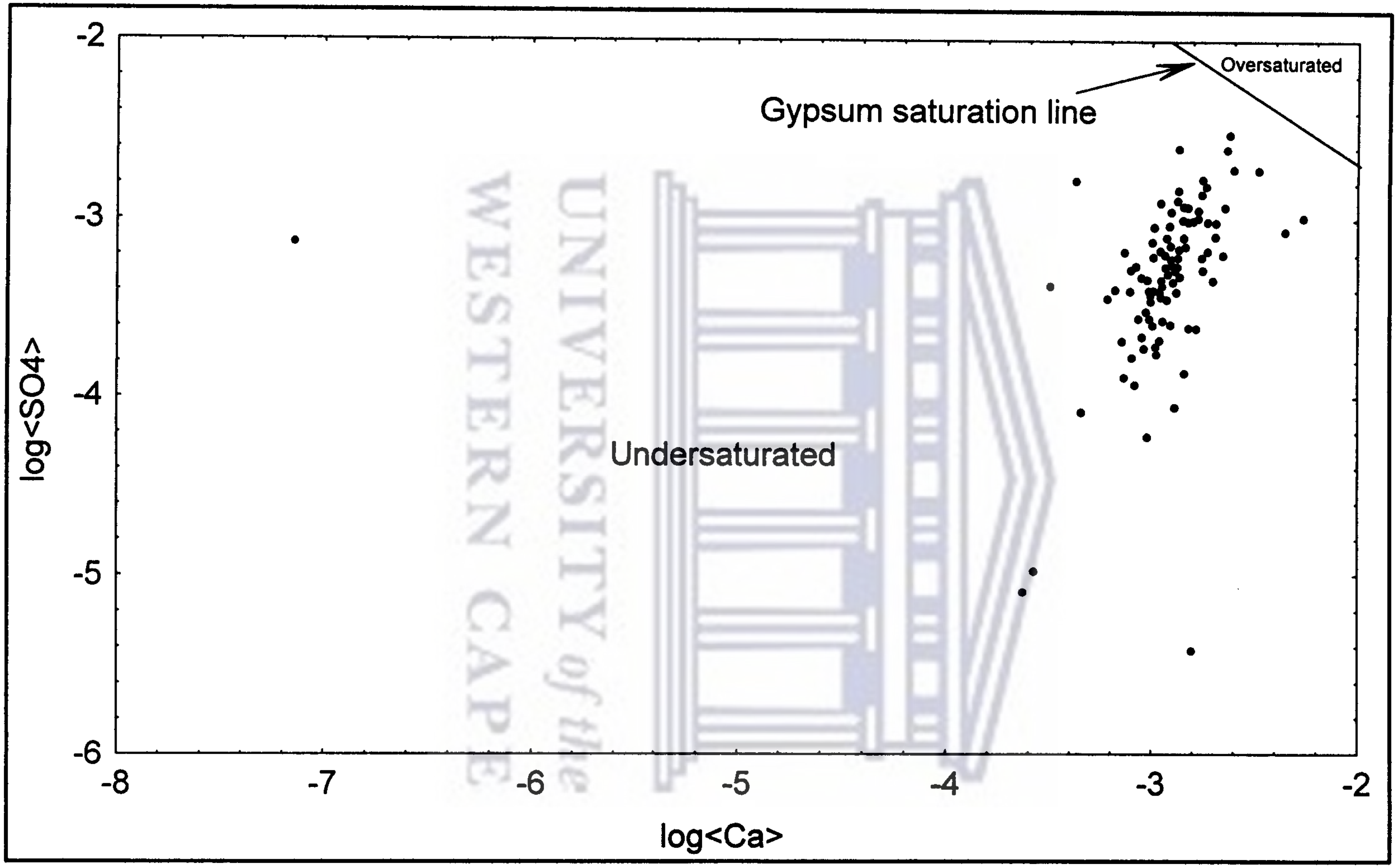


Figure 5.19. Activity-Activity diagram for gypsum saturation.

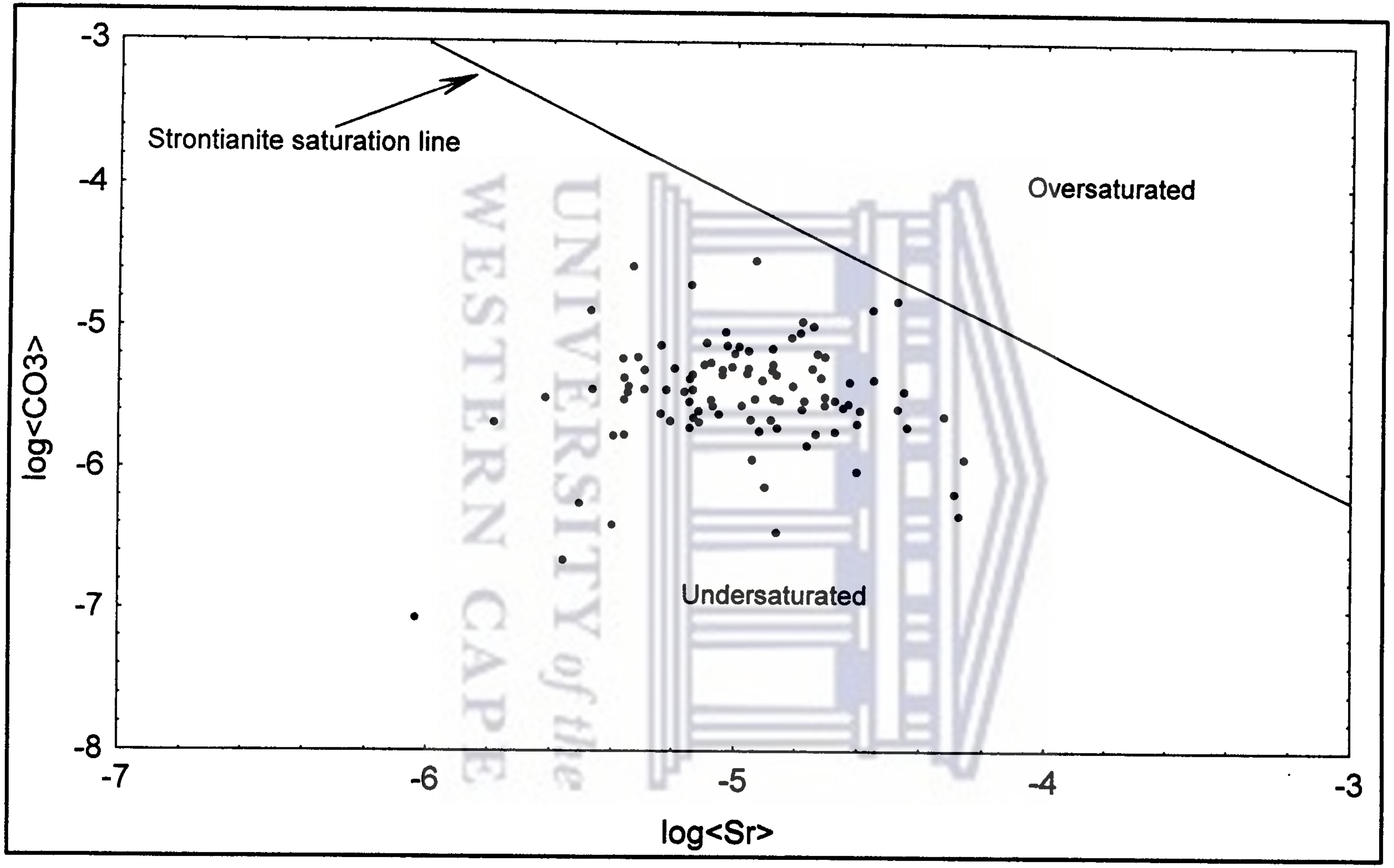


Figure 5.20. Activity-Activity diagram for strontianite saturation.

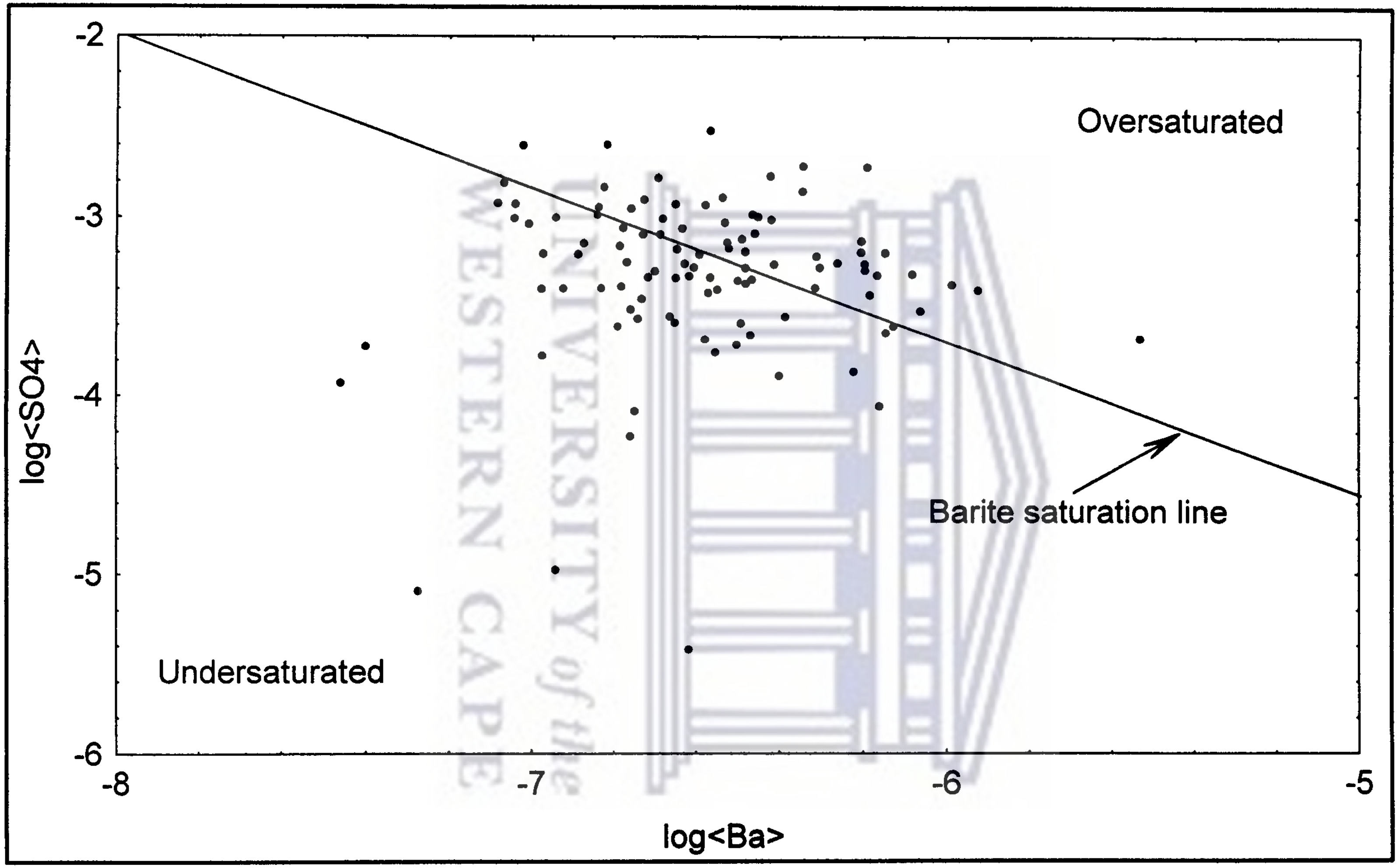


Figure 5.21. Activity-Activity diagram for barite saturation.

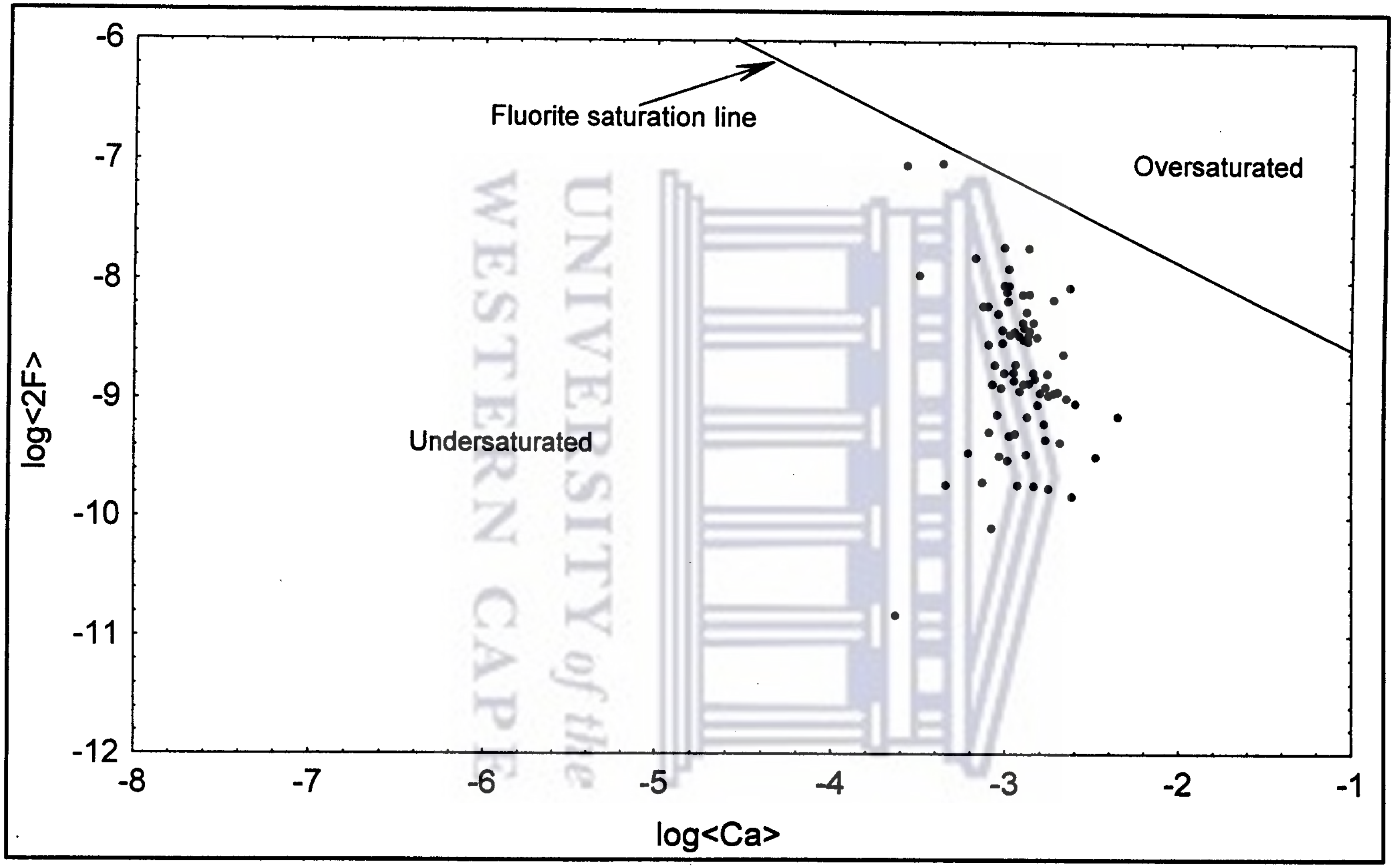


Figure 5.22. Activity-Activity diagram for fluorite saturation.

The statistical analysis showed that the main ions involved in cation exchange reactions are:

Na-Ca; Na-Mg; Sr-Ca; Sr-Mg, Sr-Na and K-Na.

The correlation matrices produced for the data set (Table 5.2) indicate that the cations all correlate positively. However, cation exchange processes require that the major exchangeable ions should correlate negatively (i.e. an ion should increase at the expense of another cation). The signatures of the various chemical processes, including cation exchange are masked by other effects, eg. evapotranspiration. Cation exchange processes in the groundwaters of the study area should preferably not be sought in a data set covering a complex area due to the heterogeneity of the aquifers.

A borehole, situated in a valley and used for irrigation, was pumped for four (4) hours and sampled over the four-hour period (Plate V, p114). The chemical results of this borehole (HEB6) are given in Appendix V. Water is pumped by means of a mono-diesel pump with a flow rate of approximately 2 *l/s*. A definite change in chemistry over time occurs. The assumption can be made that the groundwater, as it is extracted over time, becomes progressively more representative of deeper water. The temperature of the water tends to increase as time progresses.

On a Piper diagram (Figure 5.23) the change in chemistry of the groundwater is evident with the increase in Na+K and the subsequent decrease in Ca+Mg. The percentage anions in the anion triangular field of the Piper diagram remains fixed whilst in the cation triangular field there is a gradual change of the cations towards the Na+K corner of the diamond field (i.e. Ca and Mg are decreasing at the expense of Na+K). This could be attributed to the effect of cation exchange, where Ca+Mg is adsorbed by the aquifer matrix and replaced by Na+K in the subsurface waters with an increase in depth or increase in time. This decrease in Ca+Mg causes the equilibrium of Ca-Mg-H_2CO_3-$CaCO_3$ to become disturbed with the subsequent dissolution of additional calcite. The Ca is also exchanged for Na with a concurrent increase in pH and Na (Tredoux and Kirchner, 1981). There is thus a definite change in the chemical character of the water with depth. It is also evident that the role of cation exchange is significant in the fractured aquifers around Sutherland.

The character of this specific water can either be described as a deeper, older water with the top part of the water body being a more freshly mixed water as a result of infiltration or a water having a different origin and thus a different character flowing over a more saline water. The latter is not favoured due to the fact that the isotopic differences of both ^{18}O and ^{2}H of a sample taken at 1 minute after pumping started and a sample taken after 240 minutes (Table 5.9) does not differ significantly.

Table 5.9. Isotopic composition of groundwater of the same borehole pumped over a four (4) hour period.

Sample no.	δOxygen-18	δDeuterium	Time (min)
Heb 6.1	-5.5	-38	1
Heb 6.2	-5.4	-36	240

This chemical behaviour of the HEB6 borehole indicates that the groundwaters undergo chemical alteration by means of cation exchange with depth. Cation exchange is more pronounced deeper within the aquifer. This is accompanied by an increase in the electrical conductivity with depth.

5.5.4 Influence of human activities and land use on the groundwater chemistry.

Groundwater changes occur because of natural processes or through the activities of man. Land use practises in the study area has changed due to the electrification of the area. Expansion of the electricity supply resulted in massive groundwater exploitation due to the installation of high yielding pumps. The usage of diesel pumps also contributes significantly to the exploitation of the groundwater resources. The higher yielding pumps also mean that larger areas can be irrigated. Flood irrigation is the predominant type of irrigation used to water fields (Plate VI, p114).

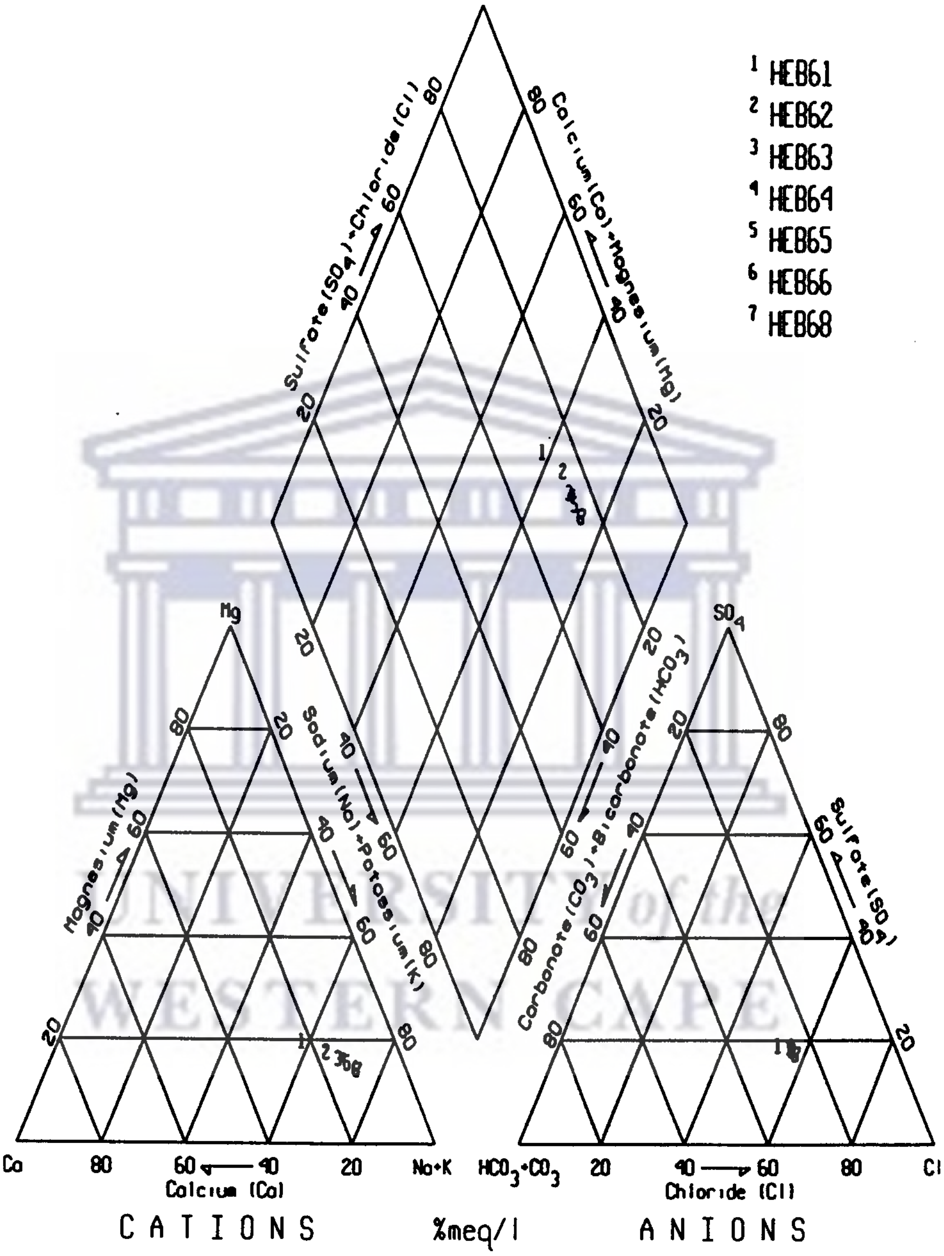


Figure 5.23. Piper diagram for borehole HEB6.

Currently no agricultural chemicals are used to fertilise fields and only crops that can withstand the soil conditions and water quality are planted. Flood irrigation of fields coupled with the high evapotranspiration rate of the area result in the salinisation of the soil. During events of recharge or infiltration, the salts are leached towards the water table and finally to the groundwater body. Thus, irrigation water that is being extracted and used for irrigation is contributing to the groundwater salinity. This effect could be similar to water being discharged, naturally, at some point (i.e. rivers and springs). Zones displaying high salinity waters occur where these irrigated areas are found. Areas that are possibly influenced by salinisation of the groundwater due to irrigation practices have very high total dissolved solids concentrations in the range of 1175 - 5468 mg/l. It is difficult to distinguish between the contributions of natural salinisation and the effect of the irrigation on the groundwater composition.

The predominant agricultural activity in the area is livestock farming. Most of the boreholes sampled in the area are used for livestock watering. Watering points and feedlots are usually situated near the boreholes. Due to the absence of buffer zones, boreholes are susceptible to pollution. High levels and sporadic occurrences of nitrates is a possible indicator of pollution, specifically point source pollution. Sources of nitrate in the area may be due to the presence of nitrogen in the soils and animal wastes. Livestock excrement contains more or less 5% nitrogen of its dry mass, mostly in the form of urea which is hydrolysed and decomposes to ammonia (Alexander, 1961). Tillage of fields may also be a source of nitrogen.

Nitrate concentration varies between 0 - 37.2 mg/l (mean 4.74 mg/l). No geologic origin of nitrate is possible within the rock formations (Tredoux, 1993). The main process that may concentrate NO_x - N is evaporation. Because of its low adsorption potential, which is due to its negative ionic charge, nitrate is easily leached out of the surface soil mixing zone by water (Shirmohammadi et al, 1991).

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 INTRODUCTION

The chemistry data of the study area's groundwater was subjected to statistical (descriptive, correlation matrices and factor analyses), graphical (Stiff, Piper and hydrogeochemical maps) and hydrogeochemical (isotopes and saturation state calculations) analyses to elucidate the groundwater chemistry of the Sutherland region. The analyses defined the major constituents, factors and processes responsible for the chemical composition of the groundwater of the area. Hydrogeochemical and spatial analyses were performed based on the statistical analyses to test the validity of the statistical analyses and to explain the correlations and processes defined.

The conclusions are discussed in terms of the objectives. All of the objectives as outlined in Chapter 1 have been met.

6.2 CHEMICAL COMPOSITION OF THE GROUNDWATERS

In order to determine the chemical composition of the groundwater a wide spectrum of elements was analysed for. This was important in order to establish the groundwater chemistry and to utilise the data in the modelling program (NETPATH), through a WATEQF subroutine (Plummer et al., 1992). From the statistical analyses it was determined that the groundwater chemistry of the area is dominated by the ions Na, Ca, Cl, HCO_3 and SO_4. The major water types of the area as determined from Stiff diagrams, are Na-Cl, Na-HCO_3, Ca-HCO_3, Ca-Cl, Ca-SO_4 and Na-SO_4. An isotopic analysis on some of the groundwater samples revealed that most of the water that is recharged is evaporated surface waters that undergo chemical changes in the subsurface.

6.3 IDENTIFICATION AND INTERPRETATION OF THE GROUNDWATER CHEMISTRY.

The chemical composition of the groundwater evolves from a Ca-HCO_3 type to a Na-Cl type water. The Ca-HCO_3 water is much fresher than the next water type as it evolves. Thus, an increase in the mean TDS occurs as the water evolves according to the sequence indicated below.

$$\text{Ca-HCO}_3 \rightarrow \text{Na-HCO}_3 \rightarrow \text{Ca-SO}_4 \rightarrow \text{Na-SO}_4 \rightarrow \text{Ca-Cl} \rightarrow \text{Na-Cl}$$
$$\rightarrow \text{Increase in TDS} \rightarrow$$

The sequence emulates the flow path sequence formulated by Chebotarev (Freeze and Cherry, 1979). The above sequence tends to evolve over very short flow paths in the study area. The main factors that determine the groundwater composition are the topography, the arid nature of the study area, the geology and the anthropogenic activities occurring in the area.

The following processes mainly control the chemical composition of the groundwater:

(1) Aquifer replenishment by precipitation, charged with CO_2, possibly occurs along preferred pathways. In topographic higher lying areas this infiltrated water dissolves mostly, carbonate minerals. In topographic lower lying areas, the leaching of soluble evaporitic salts in the unsaturated zone and the infiltration of evaporated water are the dominant processes. However, the direct infiltration of precipitation in lower lying areas could also occur, leading to processes occurring in higher lying areas. These processes are, therefore, responsible for Ca-HCO_3 type waters in higher lying areas and flatter areas where direct infiltration occurs. Sodium-chloride waters are formed in lower lying areas where salt accumulation in the unsaturated zone is prevalent.

(2) The processes of dissolution, precipitation and cation exchange primarily

control the formation of water types that evolve between the Ca-HCO_3 and the Na-Cl type waters. Cation exchange processes are mainly responsible for the formation of Na-HCO_3 waters in both surface and subsurface waters. Dissolution and precipitation of mineral phases determine the contribution and removal of ionic species in solution. Precipitation of calcite disrupts the Ca concentration equilibrium in solution, which leads to the dissolution of minerals (i.e. gypsum) containing ions that can replace the precipitated elements. The formation of Ca-SO_4 type waters is possibly formed this way. The process of cation exchange may also be responsible for the formation of Na-SO_4 type waters. Reverse cation exchange is evident in the formation of Ca-Cl type waters by which attached Ca is exchanged for Na. The formation of Ca-Cl type waters is possibly an indication of a process of refreshening of older, more saline waters with fresher Ca-type water.

6.4 HYDROGEOCHEMICAL MAPPING

The hydrogeochemical maps produced for the area clearly indicates the effect of the topography, whereby contours of high concentrations plot in local depressions such as flat plains, valleys and rivers. Topographically flat areas yield the poorest quality groundwaters as opposed to areas in topographically higher and steeper areas, which have a relatively better quality groundwater. However, the amount of data points, especially the northern part of the study area, influences the quality and reliability of the hydrochemical contours.

6.5 PHYSICAL CONDITIONS DETERMINING THE CHEMICAL VARIABILITY OF THE GROUNDWATERS.

Topography has been identified as the primary variable that influences the quality of the groundwater. Lower lying areas generally yield the poorest quality water. Groundwater flow in flatter areas is slow to static and residence times are increased, together with the addition of saline waters from surface recharge are primarily responsible for the Na-Cl type waters.

The geological materials are the major source and control of solutes. The influence of the geological materials on the groundwater chemistry is masked by the high salinity of the waters. The major influence on the chemistry of the groundwater results from the infiltration of evaporated surface water and the leaching of soluble salts in the unsaturated zone. This is verified in the statistical, hydrochemical and isotopic analyses. Areas in which high concentrations of especially the trace elements are expected (i.e. along the various igneous intrusions) do not show any anomalous trends. This is an indication that the relation has been lost or that the minerals that make up these rocks, are not very reactive. The intrusions and the associated fractures serves only as high conduit units for groundwater flow.

Superimposed on the effects of topography and geochemistry of the subsurface waters, are the influences of man. Both factor analyses and the isolated spatial occurrences of nitrates, manifested in the hydrochemical contour maps, identified the influence of anthropogenic activities as a major source of pollution.

This hydrogeochemical study of the Sutherland region illustrates the suitability of using simple statistical techniques together with graphical methods and hydrogeochemical techniques to characterise the groundwaters. However, it must be emphasised that not all the processes identified govern the chemical character of the groundwater. Determination of oxidation-reduction processes has not been included in this study. Sulphate reduction is an important process occurring in the groundwater in the Sutherland region and is manifested by the production of hydrogen sulphide gas. Hydrogen sulphide gas (H_2S) is responsible for giving most of the water of the region a foul smell.

6.6 RECOMMENDATIONS

Insufficient information on the vertical geology of the area severely hampered most of the interpretations. Drilling of boreholes, determining the exact geological profiles and sampling the boreholes at specific lithological units, might unravel the geological influences on the groundwater chemistry. The development of a test site similarly to the Agter-Witzenberg study site (Weaver et al., 1996) on a micro-catchment is proposed.

From this study, it is evident that boreholes situated in areas where evaporation is high, usually in flat plains, the quality of the water causes it to be unsuitable for usage. Water of better quality would thus generally be found in topographic higher lying locations. These locations should be targeted for developing boreholes that could yield a relatively better quality of water.

From a management perspective, it is recommended that a monitoring program be initiated. Currently, the production boreholes of the area are not being monitored. A monitoring program, on a micro-catchment scale, could identify the effects of abstraction on the groundwater quality as well as determine the seasonal influences on the groundwater quality. Implementation of borehole protection zones may prevent the infiltration of pollutants to the subsurface.

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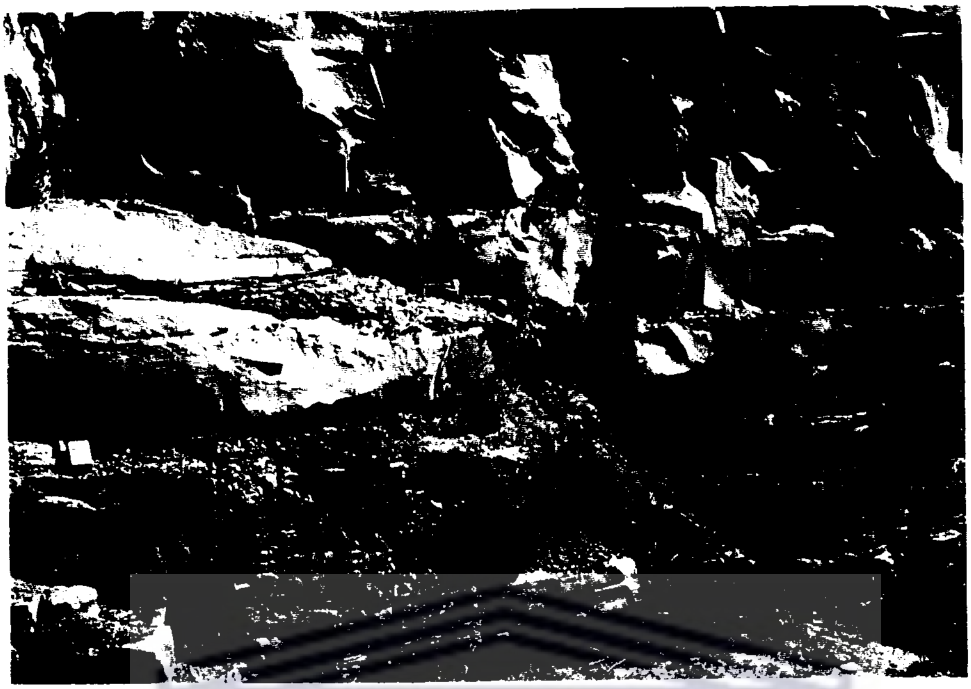

Plate I. Sedimentary rocks of the Abrahamskraal formation.

Plate II. Artesian well in dolerite on the farm Eseljacht.

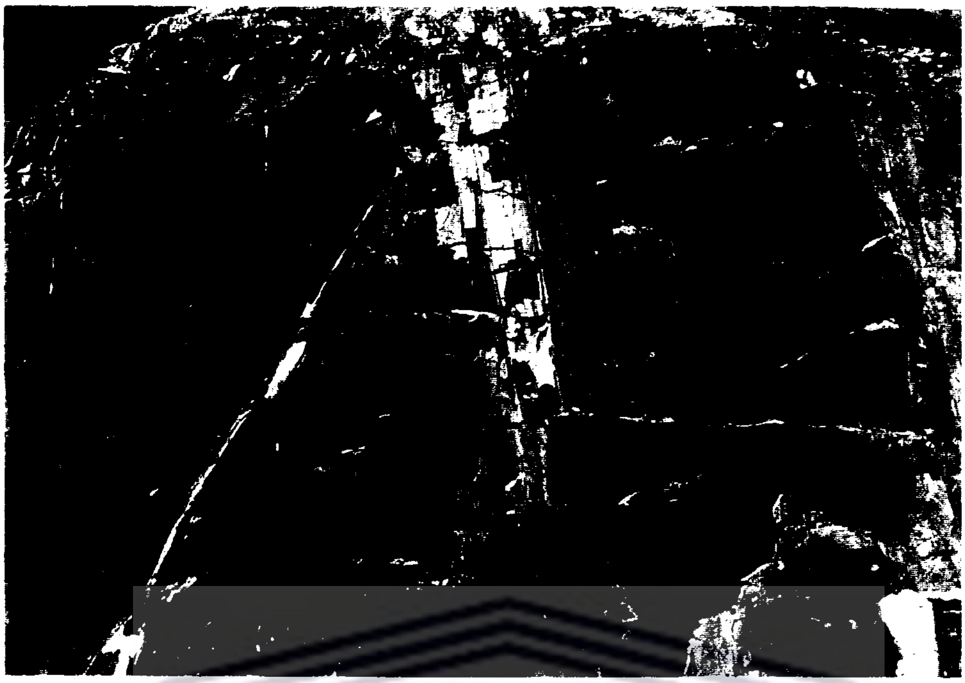

Plate III. Fractured sedimentary rocks of the study area.

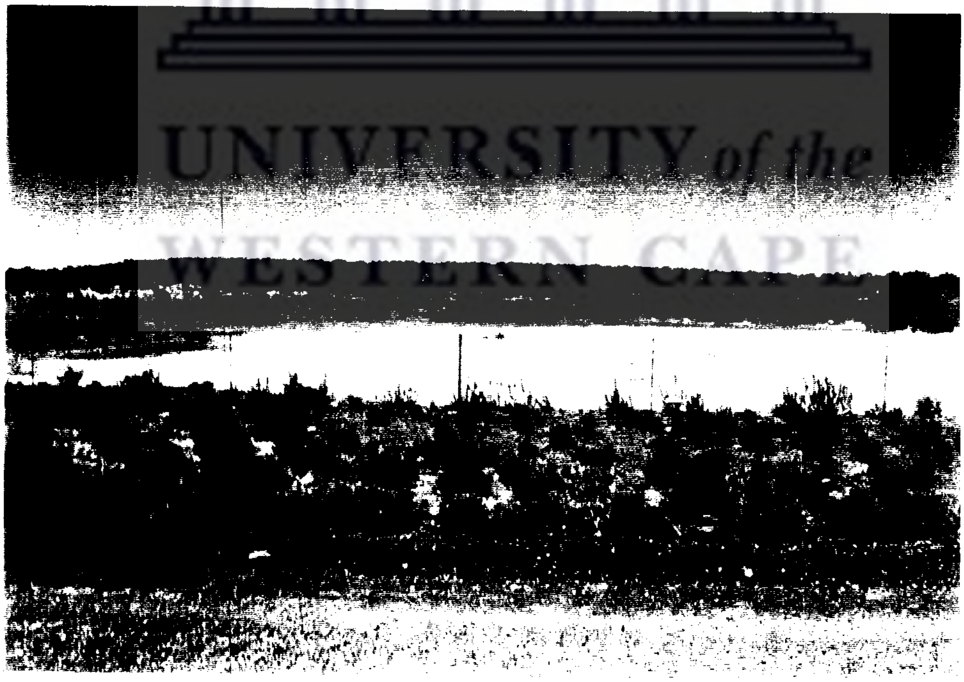

Plate IV. Salt accumulation in flat plains.

Plate V. The borehole, HEB6 that was pumped for four hours.

Plate VI. Flood irrigation to water fields.

APPENDIX I

Precipitation chemistry data set

RAINWATER AND SNOWMELT CHEMISTRY

TYPE	LOCALITY	pH	EC (mS/m)	HCO_3	Cl	SO_4	Ca	Mg	Na	K	Ba	Ni	Sr	Cu	Mn	Zn	B	P	TDS
Rain	Sutherland	5.2	0	6.2	0.87	0.814	0.214	0.03	0.151	0	0	0.02	0.02	0	0	0	0	0.13	8.453
Snow	Sutherland	6.13	2.9	9.3	0.87	4.189	2.694	0.226	1.606	0.635	0.01	0	0.06	0.01	0	0	0	0.19	19.797
Rain	De Vrede	5.7	2.28	6.2	8.7	0.674	0.523	0.179	0.358	0.55	0	0.03	0	0.01	0	0	0	0.11	17.339
Rain	Sutherland	5.27	0	13.54	8.64	0.233	0.03	0.01	0.08	0.163	0	0	0	0	0	1.443	0	0	24.148

All values in ppm, unless otherwise indicated.

APPENDIX II

Surface water chemistry data set

SURFACE WATER CHEMISTRY																						
ID	pH	EC(mS/m)	HCO_3	SO_4	F	Cl	NO_3	Ca	Mg	Na	K	Al	Ba	Ni	Sr	U	Cu	Mn	Zn	B	P	TDS
Rivbas	7.15	31	152.35	10.32	0.1	43.1	0	29.8	13.97	18.03	4	0	0	0	0.12	0	0	0	0	0.02	0	272
Renriv	6.45	43	148.96	15.63	0.3	69	0	26.9	12.21	51.71	10.4	0	0	0	0.33	0	0	0	0	0.06	0	336

All values in ppm, unless otherwise indicated.

RIVBAS - TRIBUTARY
RENRIV - MAIN RIVER

APPENDIX III

Physical, hydrochemical and isotope data set

GROUNDWATER DATA - SUTHERLAND REGION

SITE	LATITUDE	LONGITUDE	TOPOGRAPHY	GEOLOGY	FRACTURE	DIRECTION	$H_2$0 LEVEL(m)	DEPTH(m)	H_2O TYPE
Rhoog 1	-32.3089	20.51083	flat	sandst.	dol	nw			CaHCO3
Swart 3	-32.2614	20.92417	flat	sandst.	carb.	ne			NaCl
Kuil 9	-32.4089	20.88694	flat	sandst.	car/kim	ne/e-w	10.25	33.51	NaHCO3
Klip 12	-32.4003	20.70389	flat	sandst.			11.8	30.4	NaHCO3
Brak 2	-32.48972	20.720833333	flat	sandst.	carb.	ne	15.4	41.2	CaCl
Brak 4	-32.46806	20.7175	flat	sandst.		ne			NaCl
Port 1	-32.48389	20.912777778	flat	sandst.	carb.	e-w			NaHCO3
Port 4	-32.52611	20.900555556	flat	shale	carb.	ne			NaCl
Port 8	-32.53806	20.87675	flat	sandst.	carb.				NaHCO3
Sal 1	-32.5	20.820277778	flat	sandst.	carb.	nnw			NaCl
Hard 1	-32.50611	20.785277778	flat	carb.	carb.	ne	5.9	43.25	NaCl
Hard 3	-32.51944	20.79	flat	sandst.	dol/car	n-s/ne	6.22	19.52	NaCl
Jak 1	-32.48861	20.654166667	flat	sandst.	dol/car	ne	30.33		NaCl
Kuil 1	-32.42083	20.796388889	flat	sandst.					NaCl
Elim 1	-32.41778	20.964722222	flat	shale/ss	dol	nnw			NaCl
Boes 5	-32.42139	20.948888889	flat	sandst.	car/kim	e-w/ne			NaHCO3
Klip 5	-32.38833	20.716111111	flat	sand/dol	carb.	ne			NaHCO3
Rooi 6	-32.46778	20.650833333	flat	sandst.					NaCl
Rooi 7	-32.43833	20.656666667	flat	sand/dol	dol/mj	e-w/e-w			CaHCO3
Vol 3	-32.30667	20.806666667	flat	sand/dol	dol/car	ne			CaCl
Ou 1	-32.3975	20.640833333	flat	sand/dol	carb.	ne			NaCl
Har 1	-32.39222	20.525	flat	shale/ss	basalt				CaHCO3
Har 2	-32.405	20.523333333	flat	sandst.					NaCl
Geel 3	-32.4425	20.541666667	flat	sandst.	dol	e-w			CaCl
El 1	-32.51278	20.54	flat	sandst.					CaSO4
El 4	-32.48778	20.526666667	flat	sandst.					CaCl
Fon 2	-32.52167	20.63	flat	sandst.	mj	e-w			CaCl
PA 1	-32.5	20.646666667	flat	sandst.	carb.	ne			CaSO4
Guns 8	-32.55083	20.674444444	flat	sandst.					NaCl
Brink 1	-32.30417	20.669166667	flat	sandst.	carb.	ne			CaCl
Brink 2	-32.30222	20.690555556	flat	sandst.					NaCl

GROUNDWATER DATA - SUTHERLAND REGION

SITE	LATITUDE	LONGITUDE	TOPOGRAPHY	GEOLOGY	FRACTURE	DIRECTION	H_20 LEVEL(m)	DEPTH(m)	H_2O TYPE
Man 1	-32.22222	20.687777778	flat	sandst.					NaCl
KK 1	-32.28111	20.579722222	flat	sandst.					CaCl
Twee 3	-32.06917	20.5375	flat	sandst.					NaCl
MR 1	-32.21778	20.52	flat	sandst.			15	35	NaCl
MR 2	-32.22	20.521944444	flat	sandst.					NaHCO3
MR 3	-32.22083	20.493888889	flat	sandst.					NaCl
Ber 1	-32.02889	20.9525	flat	sandst.			5.9	36.5	CaHCO3
Bav 1	-32.05	20.938888889	flat	sandst.	dol	n-s/e-w			NaCl
Bav 2	-32.05833	20.9475	flat	sandst.					NaCl
Pal 2	-32.20417	20.836666667	flat	sand/dol					CaHCO3
Swart 2	-32.25417	20.855555556	flat	sandst.	kimb	ne			NaCl
Dut 1	-32.49056	20.648055556	flat	sandst.					CaCl
ROD 1	-32.31694	20.899722222	flat	sandst.					CaHCO3
Vred 3	-32.52	20.84472	foothill	sandst.					CaHCO3
Font 1	-32.25028	20.875277778	foothill	sandst.	carb.	ne			
Pan 2	-32.30528	20.600833333	foothill	shale/ss	dol	ne			NaCl
Vyf 6	-32.39333	20.540555556	foothill	sandst.			16.5	27	CaCl
RK 1	-32.25361	20.7075	foothill	sandst.					NaHCO3
Kuil 15	-32.40722	20.838333333	hill	shal/dol	dol	nw	20.15	48.9	NaHCO3
Mid 5	-32.39028	20.6675	hill	sandst.	dol		32	37.95	CaHCO3
Jak 5	-32.48472	20.673333333	hill	dol			23.5	42	CaHCO3
RD 1	-32.18861	20.6075	hill	dol					NaHCO3
RD 2	-32.25167	20.588611111	hill	sandst.					CaHCO3
Pal 1	-32.18611	20.838888889	hill	sandst.					CaHCO3
Hot 1	-32.46667	20.535555556	hill	sandst.					CaHCO3
Kook 1	-32.54056	20.938055556	river	sandst.	carb.	ne/nw			NaCl
Vred 11	-32.56111	20.835	river	sandst.	mj	ne/nnw	1.34	15	CaHCO3
Sal 5	-32.46083	20.835833333	river	sandst.	carb.				NaHCO3
Kuil 6	-32.42806	20.841388889	river	shale/ss					NaHCO3
Sut 1	-32.39556	20.663611111	river	sandst.				133.33	NaSO4
Blyd 6	-32.40361	20.989722222	river	shale/ss	carb.	ne			NaCl

GROUNDWATER DATA - SUTHERLAND REGION

SITE	LATITUDE	LONGITUDE	TOPOGRAPHY	GEOLOGY	FRACTURE	DIRECTION	H_20 LEVEL(m)	DEPTH(m)	H_2O TYPE
PA 2	-32.55139	20.6225	river	sandst.					CaCl
PA 4	-32.56833	20.556111111	river	sandst.					CaHCO3
Uit 3	-32.19	20.713333333	river	sandst.					NaHCO3
Sny 1	-32.03111	20.640555556	river	sandst.					NaCl
Sny 4	-32.05389	20.656388889	river	sandst.					Ca-HCO3
Haak 1	-32.07389	20.658055556	river	sandst.					CaSO4
Stof 2	-32.15944	20.723611111	river	sandst.				32	CaCl
Stof 3	-32.15806	20.724722222	river	sandst.					CaCl
RW 1	-32.025	20.524166667	river	sandst.					NaCl
Druip 1	-32.13611	20.614166667	river	sandst.					NaHCO3
Wil 1	-32.30556	20.842222222	river	sand/dol					Ca-HCO3
Mar 6	-32.35417	20.684722222	river	sandst.	dol	nw			CaCl
Sal 2	-32.4764	20.83333	slope	sandst.	carb.	nw			NaHCO3
Bron 3	-32.3181	20.67111	slope	sandst.					NaCl
Kuil 14	-32.4064	20.84666	slope	sandst.	dol	nw			NaHCO3
Vred 2	-32.54444	20.835	slope	sandst.	carb.	ne	6.9	45.32	NaHCO3
Vred 10	-32.52528	20.823888889	slope	sandst.	carb.	ne/nw	3.1	56.5	Ca-HCO3
Vred 12	-32.56889	20.789444444	slope	sandst.	carb.	ne	6.57	22	NaHCO3
Kuil 7	-32.42139	20.845555556	slope	shale	dol/kim	nw/ew			NaHCO3
Sut 2	-32.40944	20.664444444	slope	sandst.				93.33	NaHCO3
Blyd 1	-32.38639	20.964722222	slope	sandst.	car/kim	e-w/ne			NaHCO3
Welt 6	-32.32611	20.555277778	slope	sandst.					Ca-HCO3
Welt 7	-32.32	20.5475	slope	shale/ss	dol	nw	2	41.66	Ca-HCO3
Geel 2	-32.42833	20.55	slope	sandst.					NaCl
Hoek 1	-32.45028	20.588611111	slope	sandst.	dol	n-s			Ca-HCO3
Guns 2	-32.58389	20.689444444	slope	sandst.	carb.	ne	1.52	29	NaHCO3
Eland 6	-32.385	20.937222222	slope	sandst.					Ca-HCO3
Eland 7	-32.365	20.674444444	slope	dol					Ca-HCO3
Bas 1	-32.09917	20.666666667	slope	sandst.					Ca-HCO3
SK 1	-32.15556	20.883611111	slope	sandst.					Ca-HCO3
Sout 4	-32.47083	20.958333333	valley	shale	carb.		7.72	31	NaCl

GROUNDWATER DATA - SUTHERLAND REGION									
SITE	LATITUDE	LONGITUDE	TOPOGRAPHY	GEOLOGY	FRACTURE	DIRECTION	$H_2$0 LEVEL(m)	DEPTH(m)	H_2O TYPE
Sout 2	-32.48917	20.956111111	valley	shale	carb.	e-w	18.33	40	NaHCO3
Lang 3	-32.3839	20.75778	valley	sandst.					NaHCO3
Rhee 1	-32.3242	20.50139	valley	sandst.	dol	nnw			Ca-HCO3
Heb 6	-32.3422	20.87444	valley	sandst.	carb.	ne			NaCl
Bron 4	-32.30722	20.688333333	valley	shale					NaCl
Jag 2	-32.34306	20.585277778	valley	dol			0		Ca-HCO3
Heb 2	-32.34194	20.868611111	valley	shal/dol					Na-HCO3
Vyf 2	-32.40278	20.578888889	valley	sandst.	dol	ns/ew			CaCl
Vyf 5	-32.37611	20.571111111	valley	sandst.	dol	ns			CaSO4
Bok 1	-32.44417	20.789444444	valley	sandst.		e-w	14.12	43.56	NaCl
Twee 1	-32.07	20.5125	valley	sandst.			5.9	25.3	Na-HCO3
Twee 2	-32.05806	20.546666667	valley	sandst.					Na-HCO3
Twee 4	-32.12	20.539444444	valley	sandst.	dol				Na-HCO3
Eend 1	-32.23389	20.978333333	valley	sandst.	kimb	e-w			NaCl
Swart 1	-32.23639	20.902777778	valley	sandst.	dol/kim	n-s/e-w			Na-HCO3

dol = dolerite
shal = shale
sandst. = sandstone
kim(b) = kimberlite
car(b) = carbonatite

GROUNDWATER CHEMISTRY - FIELD DETERMINANTS (except pCO_2)

SITE	pCO_2 (atm)	pH	EC(mS/m)	Eh (mV)	Temp.(°C)	Alk.	SITE	pCO_2	pH	EC	Eh (mV)	Temp.	Alk.
Rhoog 1	0.03399	6.9	140.1	-1	21	264	Pal 1	0.0128	7.35	57.6	-19.1	21	234
Swart 3	0.02112	7.17	194.1	-9.9	18.3		Hot 1	0.0071	7.411	62.6	-20.3	20.1	
Kuil 9	0.0219	7.27	140.5	-15.8	17.3		Kook 1	0.0078	7.5	166	-34.4	15.2	
Klip 12	0.0153	7.33	112	-19.4	18.5		Vred 11	0.007	7.5	59	-7.5	17	
Brak 2	0.02891	6.7	395	11.3	15		Sal 5	0.0053	7.8	104	-31.8	14.6	
Brak 4	0.0266	6.8	986	3.9	14.1		Kuil 6	0.01214	7.4	122.8	-16.1	17.3	
Port 1	0.0338	7.14	191	-8.3	19.6		Sut 1	0	8.5	123.6	-71	17.6	
Port 4	0.01281	7.4	200	-26.6	14.5		Blyd 6	0.0055	7.7	183	-36.9	19	
Port 8	0.00522	7.7	95	-41.2	9.8		PA 2	0.01585	7.164	89.9	-8.9	17.6	
Sal 1	0.00683	7.5	457	3.6	13.9		PA 4	0.01049	7.3	84.7	-19	20.7	
Hard 1	0.00251	7.8	96	-29.8	5.9		Uit 3	0.02052	7.2	114.5	-15.4	21	262
Hard 3	0.03235	7.1	502	11.6	14.1		Sny 1	0.03949	7.058	252	-4	19.2	
Jak 1	0.00404	7.5	121	-29.7	15.5		Sny 4	0.01853	7.2	96.7	-7.8	20	230
Kuil 1	0.0094	7.4	150.8	-14.5	16.8		Haak 1	0.0073	7.4	114.5	-21.1	18.3	550
Elim 1	0.01656	7.4	182.4	-12.5	20.7		Stof 2	0.02264	7.082	179.4	-4.9	19.5	241
Boes 5	0.00569	7.8	133.6	-38	21.5		Stof 3	0.03474	6.96	209	0.8	19.7	294
Klip 5	0.00972	7.5	124.9	-20.8	19.4		RW 1	0.02116	7.2	184.5	-16.1	21.1	314
Rooi 6	0.00957	7.3	165.2	-5.2	15.1		Druip 1	0.02173	7.2	137.7	-12.7	18	422
Rooi 7	0.01126	7.3	59.1	-5.7	18.2		Wil 1	0.01073	7.408	95.4	-23.9	19.8	220
Vol 3	0.02765	7	391	3.9	18.5		Mar 6	0.01459	7.363	163.8	-20.1	20	280
Ou 1	0.00976	7.2	133.4	2.1	24.1		Sal 2	0.0233	7.22	132.1	-12.7	17.7	
Har 1	0.0126	7.2	76.3	-18.4	20.3	190	Bron 3	0.0042	7.56	106.8	-33.3	19.3	
Har 2	0.00602	7.5	121.8	-30.7	22	197	Kuil 14	0.0262	7.16	165.7	-8.6	17.6	
Geel 3	0.00721	7.2	430	-12.9	16.2	143	Vred 2	0.02804	6.9	98	-16.4	17	
El 1	0.0146	7	158.5	-1.9	17.1	114.1	Vred 10	0.0037	7.7	67	-18.2	6	
El 4	0.03353	6.6	93.3	19.7	17.5	120	Vred 12	0.0029	8.1	113	-45.6	17.4	
Fon 2	0.01217	7.2	148.2	-12.3	16.7	195	Kuil 7	0.04151	7.03	111.2	3.3	17.3	
PA 1	0.0118	7.2	116	-9.9	17.7	148	Sut 2	0.0033	7.8	72.2	-35.9	16.2	
Guns 8	0.01064	7.3	244	-20.5	15.5	224	Blyd 1	0.0039	8	92.7	-54.9	23.8	
Brink 1	0.01569	7.3	262	-12.7	23.5	362	Welt 6	0.01509	6.8	55	17.6	17	

GROUNDWATER CHEMISTRY - FIELD DETERMINANTS (except pCO_2)

SITE	pCO_2 (atm)	pH	EC mS/m	Eh (mV)	Temp.	Alk.	SITE	pCO_2	pH	EC	Eh (mV)	Temp.	Alk.
Brink 2	0.0061	7.7	239	-43.9	18.6	329	Welt 7	0.01632	7.1	54.2	2.2	18.6	
Man 1	0.0207	7.3	252	-19	21	350	Geel 2	0.001	7.8	40.6	-44	18.6	85
KK 1	0.00993	7.3	165.9	-17.5	19.2	162	Hoek 1	0.02861	7.02	125.5	-2.6	19.3	270
Twee 3	0.02628	7.1	183	-9.5	20	360	Guns 2	0.01124	7.3	105.6	-19.4	16	265
MR 1	0.00977	7.3	147.1	-19	22	243	Eland 6	0.01079	7.5	77.6	-32.4	22.2	
MR 2	0.01314	7.3	135.8	-19.9	20.6	245	Eland 7	0.01489	7.394	83.9	-22.5	19.2	348
MR 3	0.01325	7.5	405	-27.8	23.4	420	Bas 1	0.01949	7.1	64.2	-6.1	20.8	152
Ber 1	0.01373	7.4	94.9	-25.2	22.6	410	SK 1	0.0108	7.356	67	-20	21.9	220
Bav 1	0.02064	7.256	171.5	-14.6	22.9	382	Sout 4	0.01495	7.3	184		19.8	
Bav 2	0.00611	7.6	127.6	-48.8	20.1	223	Sout 2	0.01639	7.3	150		20.8	
Pal 2	0.01288	7.384	70.1	-21.9	20.2	497	Lang 3	0.02363	7.1	147.5	-2	16.8	
Swart 2	0.00469	7.77	176.3	-45.2	20.3	350	Rhee 1	0.01535	7.2	76.9	-12.2	17.8	
Dut 1	0.03472	6.945	227	3.8	17.1	268	Heb 6	0.0523	6.869	270	15.9	15.9	
ROD 1	0.03074	7.088	140.1	-4.7	20.2	420	Bron 4	0.0081	7.5	166.9	-15.7	19.3	
Vred 3	0.02908	7.1	109.8	-7.3	18.2	320	Jag 2	0.0036	7.7	63.8	-32.6	20	
Font 1		7.3	116	-13.5	16		Heb 2	0.01635	7.4	162.8	-10.9	18.3	
Pan 2	0.00153	7.9	189.1	-34.1	16		Vyf 2	0.0082	6.8	335	22.1	19.6	
Vyf 6	0.02145	7.1	123.8	-18.4	20.3	209	Vyf 5	0.02843	6.8	187.9	19.8	17.2	
RK 1	0.00677	7.6	114.3	-35.6	21.4		Bok 1	0.02316	7.13	221	-9.3	17.5	277.6
Kuil 15	0.01854	7.2	73.3	-7.3	17.7		Twee 1	0.01738	7.3	138.1	-21.7	19.4	222
Mid 5	0.0024	7.95	44.1	-42.9	21		Twee 2	0.01325	7.3	91.6	-19.7	22	245
Jak 5	0.01248						Twee 4	0.02681	7.04	127	-5.4	19.8	
RD 1	0.02891	6.32	177.7	37.9	19.2	95	Eend 1	0.01696	7.4	200	-24	23.3	378
RD 2	0.0255	6.757	50.2	12.7	20		Swart 1	0.02317	7.184	141.3	-10.2	19.7	450

GROUNDWATER CHEMISTRY - MAJOR IONS IN PARTS PER MILLION

SITE	HCO_3	NO_3	F	Cl	SO_4	Ca	Mg	Na	K	TDS	Na%	HCO_3%
Rhoog 1	311.5	0	0.5	158.8	240.1	134	39.89	94.64	1.288	984.675	34.659	43.818
Swart 3	372.4	4.87	1.9	344	123	77.56	35.11	165.5	5.166	1131.057	58.255	44.01
Kuil 9	487.5	11.96	1.8	158.8	75.22	57.34	37.89	185.8	4.431	1021.871	64.897	66.301
Klip 12	379.2	0	2.1	141.1	49.59	66.73	9.341	163.2	1.261	815.747	67.265	66.295
Brak 2	185.3	0		1132.3	159.9	290.9	90.68	297	1.367	2168.234	43.036	12.541
Brak 4	261	11.51		2923	462.9	633	351.2	807.4	3.103	5468.539	44.636	7.134
Port 1	563.6	2.21		244.3	232.1	121.3	82.16	196	2.259	1445.792	48.618	54.077
Port 4	407.7	0	2.6	340.3	187	83.21	29.98	328.2	5.374	1388.163	72.913	43.483
Port 8	339.7	4.87		87.3	114.4	81.28	20.29	97.07	4.115	750.828	47.574	62.185
Sal 1	300.9	0		1221.6	443	185.8	115.3	640.7	11.77	2927.54	66.712	15.309
Hard 1	208.5	10.63		122.2	44.32	26.46	16.82	133.7	1.255	566.222	74.25	54.065
Hard 3	563.6	8.41		1064.5	494.5	185.9	125.3	772.5	18.15	3239.007	69.794	26.448
Jak 1	154.4	0		226.9	37.77	71.34	16.53	130.9	1.207	643.76	58.521	36.843
Kuil 1	290.3	0	1.4	261.3	129.5	101.1	55.44	144.7	2.605	989.365	47.208	42.535
Elim 1	494.1	0	1	296.7	180.7	118.2	67.06	191.6	3.435	1355.758	50.048	50.807
Boes 5	407.7	0	2.8	209.4	74.52	48.67	16.08	261.4	1.753	1028.403	78.389	58.711
Klip 5	358.3	5.4	1.5	152.7	115.8	91.31	17.87	180.8	2.011	929.302	61.263	56.541
Rooi 6	243.9	0	0.8	409.4	140.1	136.7	68.45	158.8	1.414	1161.494	43.276	30.71
Rooi 7	257.9	33.21	0.6	52.4	80.6	58.6	20.29	58.82	0.941	564.945	42.1	60.724
Vol 3	386.1	0	0.5	855.1	607.7	344.4	157.2	299.8	3.165	2660.506	37.014	20.877
Ou 1	169.9	19.93	0.9	296.7	93.46	80.1	46.03	127.5	2.696	838.401	49.614	29.248
Har 1	223.44	0	0.3	77.65	95	77.89	17	46.09	0.983	539.902	32.201	56.369
Har 2	213.29	0	0.6	232.94	75	91.47	18.43	113.1	0.787	749.806	49.714	40.873
Geel 3	155.73	0	0.7	1276.8	275	416.7	76.99	293.7	1.609	2510.114	36.667	9.116
El 1	179.43	0	0.7	181.18	430	215.8	18.06	85.35	4.02	1120.297	25.979	22.675
El 4	155.73	0	0.3	198.43	25	91.79	18.98	44.32	1.042	537.831	28.039	41.04
Fon 2	233.6	0	1.1	258.82	0	142.7	12.87	118.7	0.725	774.306	42.346	47.333
PA 1	223.44	0	0.3	103.53	280	137.8	24.02	62.47	0.551	835.239	27.467	36.794
Guns 8	270.84	0	0.8	500.39	225	155.4	44.26	251.4	1.58	1454.479	55.009	27.165
Brink 1	365.63	3.54	0.8	569.41	161	186.8	64.74	205.9	1.101	1564.714	44.455	33.228
Brink 2	379.18	0	2	483.14	155	153.2	45.91	225	6.5	1455.417	51.844	37.199

GROUNDWATER CHEMISTRY - MAJOR IONS IN PARTS PER MILLION

SITE	HCO_3	NO_3	F	Cl	SO_4	Ca	Mg	Na	K	TDS	Na%	HCO_3%
Man 1	490.9	31.44	0.9	379.61	338	122.9	55.04	296.3	1.942	1719.456	61.986	39.562
KK 1	236.99	7.53	0.8	345.1	100	147	41.59	95.01	2.215	979.318	32.919	34.325
Twee 3	392.72	0		284.7	220	130.6	54.8	154.4	1.664	1241.228	44.949	43.761
MR 1	220.06	0	1.3	189.8	235	117.9	10.5	168	0.799	950.838	55.351	34.057
MR 2	301.31	0	1.5	172.55	235	113	12.7	149.1	1.214	993.777	52.747	42.417
MR 3	504.44	0	2.3	741.96	680	148.1	102.3	498.9	3.54	2687.517	65.876	26.154
Ber 1	379.18	23.03	1	77.65	50	77.04	25.66	78.39	3.106	716.058	42.406	71.427
Bav 1	419.8	37.2	1.3	267.45	115	103	37.3	179.8	2.38	1165.732	55.534	49.932
Bav 2	274.23	0	2.3	224.31	69.97	21.81	9.985	209.9	0.92	816.579	85.964	48.042
Pal 2	348.71	12.4	1.3	34.51	30	67.51	16.6	54.97	2.418	569.607	38.602	81.68
Swart 2	325.01	0	1.7	276.08	105	97.91	27.06	203.6	1.673	1041.543	61.127	45.919
Dut 1	382.56	0	0.9	396.86	280	194.4	46.34	172.6	1.656	1479.507	41.221	36.08
ROD 1	436.73	14.61	1.7	172.55	145	111.6	34.66	112.9	3.23	1034.903	42.826	56.675
Vred 3	429.9	4	2	123.5	49.34	86	34.95	66.39	4.407	804.382	34.041	70.621
Font 1	419.8	15.06	1.5	129.41	85	93.81	30.42	102.8	2.639	781.781	44.552	64.508
Pan 2	154.4	0	3.2	392.6	272.1	110.4	32.88	265.8	2.259	1238.465	64.02	18.777
Vyf 6	311.47	0	0.7	215.69	50	105.9	41.420.	61.8	1.559	748.658	36.266	53.901
RK 1	304.7	0	0.9	155.29	70	77.01	32.84	96.89	1.262	740.91	46.22	57.394
Kuil 15	339.7	6.64	1.6	61.1	37.42	58.08	20.07	75.35	2.159	604.271	48.035	76.087
Mid 5	236.3	0		26.2	32.65	43.6	16.99	28.26	0.634	385.446	31.421	80.061
Jak 5	301.1	0		34.9	84.3	90.32	14.83	35.04	0.666	563.668	24.526	71.639
RD 1	64.32	6.2	0.2	25.88	1.02	11.81	5.641	14.07	0.91	131.684	43.25	65.888
RD 2	159.12	4.87	0.3	60.39	20	42.73	12.65	31.31	0.898	332.845	35.584	65.032
Pal 1	314.85	0.44	1.2	43.14	10	58.73	19.26	32.27	1.831	483.217	28.638	85.18
Hot 1	199.74	0	0.4	94.9	15	79.32	9.783	30.68	0.819	433.091	24.97	64.424
Kook 1	308.8	1.77		349	228.2	100.4	30.68	200.4	5.709	1228.095	58.993	34.784
Vred 11	225.5	4.87		52.4	36.92	57.82	11.2	52.59	2.807	445.645	41.93	70.537
Sal 5	416.9	3.99		113.4	73.49	77.1	32.35	108	5.896	836.015	47.419	68.594
Kuil 6	367.5	2.21	2.1	157.1	148.1	75.88	47.86	134.2	3.392	940.314	51.043	54.283
Sut 1	120.4	0	6.8	183.2	287.8	34.46	4.154	270.5	1.031	911.5	86.825	20.127
Blyd 6	335.1	6.64	2.3	305.4	186.9	83.59	62.29	242.6	3.034	1230.188	61.689	40.067

GROUNDWATER CHEMISTRY - MAJOR IONS IN PARTS PER MILLION

SITE	HCO_3	NO_3	F	Cl	SO_4	Ca	Mg	Na	K	TDS	Na%	HCO_3%
PA 2	270.84	0	0.7	172.55	0.7	100.5	14.47	56.78	1.987	620.908	32.339	60.892
PA 4	233.6	2.66	0.5	103.53	75	74.31	16.47	59.09	3.251	571.663	37.861	56.25
Uit 3	365.63	14.17	1.4	120.78	85	67.13	27.62	113.8	2.589	799.547	53.619	62.29
Sny 1	545.07	19.49	1	319.21	280	97.41	60.79	295.2	12.79	1632.746	63.194	46.796
Sny 4	335.16	14.61	0.4	120.78	75	70.57	39.25	60.5	1.019	717.891	35.233	61.39
Haak 1	216.67	0	0.8	120.78	200	125.4	17.46	71.75	1.223	757.024	32.869	40.255
Stof 2	328.39	6.64	0.5	327.84	185	163.1	52.71	116.4	1.363	1184.421	34.676	38.708
Stof 3	382.56	10.63	0.5	388.23	230	172.4	60.02	151.8	1.6	1399.678	39.202	37.805
RW 1	389.33	5.31	1.4	293.33	170	94.37	53.31	176.1	3.687	1188.571	53.556	45.304
Druip 1	409.65	18.16	1.3	163.92	110	92.69	35.54	128.8	2.07	963.861	49.518	58.269
Wil 1	328.4	0	0.6	138.04	55	122.9	55.04	296.3	1.942	1000.618	61.986	62.907
Mar 6	399.49	14.61	0.5	284.7	115	136.6	48.89	120.4	1.463	1123.899	38.955	49.059
Sal 2	460.4	0	3.2	141.1	77.05	70.41	41.62	137.9	5.03	939.449	53.663	67.532
Bron 3	176.1	0	1.2	229.3	92.99	54.88	17.72	164.5	1.778	740.199	68.545	35.249
Kuil 14	453.7	11.96	1.8	211.7	127.6	56.56	31.85	271.1	6.141	1174.606	73.899	56.237
Vred 2	262.5	0		122.2	64.95	79.44	21.47	96.34	5.12	654.219	47.204	58.379
Vred 10	247.1	1.33		78.5	42.17	62.88	18.57	47.03	4.403	503.912	34.987	66.947
Vred 12	437	2.66		130.9	64.65	71.1	23.21	155.1	2.958	890.016	61.008	68.796
Kuil 7	529.7	2.66	2.2	78.5	84.03	70.85	37.55	140.5	3.5	952.079	55.245	75.987
Sut 2	247.1	0	0.8	61.1	91.34	55.42	17.02	71.64	1.479	548.62	48.447	61.723
Blyd 1	416.9	0	6.6	122.2	1.717	17.87	8.137	236.8	1.4	813.357	89.397	76.158
Welt 6	108.1	0	0.4	61.1	54.35	36.04	13.96	30.76	0.519	306.177	37.598	48.27
Welt 7	231.6	0	0.5	69.8	27.22	48.81	19.56	32.44	1.11	431.919	31.645	70.369
Geel 2	71.1	4.43	2.2	440	595	222.6	14.69	274	1.299	1638.159	52.289	6.39
Hoek 1	348.71	0	0.5	163.92	125	125.2	15.42	101.1	2.542	887.219	40.688	54.646
Guns 2	267.45	0	0.6	129.41	90	85.89	4.803	117.6	0.703	700.471	55.307	54.866
Eland 6	375.79	6.64	0.5	60.39	35	69.13	30.12	46.56	1.531	627.288	31.42	78.565
Eland 7	423.19	0	0.8	43.14	55	63.46	34.15	58.92	1.233	680.915	37.174	81.051
Bas 1	270.84	5.76	0.2	60.39	20	51.47	29.96	29.82	0.598	469.468	26.607	75.825
SK 1	267.45	6.64	0.9	51.76	70	64.01	18.25	48.16	2.256	530.355	36.117	67.41
Sout 4	355.2	1.33		314.1	201.7	99.64	53.7	239.9	3.443	1272.44	60.038	40.719

GROUNDWATER CHEMISTRY - MAJOR IONS IN PARTS PER MILLION												
SITE	HCO_3	NO_3	F	Cl	SO_4	Ca	Mg	Na	K	TDS	Na%	HCO_3%
Sout 2	376.8	0		191.9	135.3	83.82	37.23	188.7	3.182	1020.803	59.662	53.523
Lang 3	358.9	0.89	1.4	194.1	123	77.56	35.11	165.5	1.556	959.96	58.959	52.912
Rhee 1	281	0	0.8	70.57	64.26	64.39	15.97	64.42	1.105	564.861	43.821	67.446
Heb 6	494.5	0	1	511.6	232.3	131.8	62.67	369.4	5.652	1812.484	64.582	39.898
Bron 4	307.3	6.64	1.5	331.6	116.8	96.54	48.79	194.8	2.144	1108.619	56.684	40.231
Jag 2	200.7	0	0.4	87.3	31.85	57.08	22.31	40.47	0.58	441.563	33.431	62.67
Heb 2	497.2	5.31	1.4	235.6	152.9	98.89	50.79	212.9	3.972	1261.578	57.76	55.714
Vyf 2	55.6	0	0.3	52.3	11.34	24.18	8.6	18.73	0.788	175.918	35.593	46.512
Vyf 5	225.5	0	0.3	114.1	738.5	238	67.81	104.9	2.155	1495.683	25.211	20.911
Bok 1	389.33	0	1	370.98	275	147.9	75.67	170.3	2.55	1434.8	42.774	37.569
Twee 1	406.26	5.76	1.3	189.8	90	93.09	40.96	110.1	11.99	952.238	42.732	58.613
Twee 2	291.15	7.97	1	120.78	50	57.41	31.6	70.93	1.974	633.682	43.669	61.828
Twee 4	338.55	18.16	1.4	172.55	90	79.87	34.07	116.6	1.231	853.914	50.091	54.547
Eend 1	487.51	1.77	1.5	362.35	155	111.7	60.56	202.6	1.519	1386.8	53.574	48.358
Swart 1	413.03	16.39	0.8	215.69	100	89.08	41.6	131.6	2.328	1011.719	49.572	55.373

GROUNDWATER CHEMISTRY - TRACE ELEMENTS IN PARTS PER MILLION

SITE	Al	Ba	Ni	P	Sr	B	U	Cu	Mn	Zn
Rhoog 1	0	0.034	0	0.194	3.244	0.175	0.243	0.005	0.062	0
Swart 3	0	0.025	0	0.39	0.762	0.272	0.098	0.004	0	0
Kuil 9	0	0.024	0	0.055	0.839	0.154	0	0.012	0.007	0.039
Klip 12	0	0.089	0	0.649	2.092	0.364	0	0	0	0.031
Brak 2	0	0.165	0	0	10.18	0.327		0.006	0.109	0
Brak 4	0	0.132	0.013	0.135	14.15	0.614		0.012	0.269	0.101
Port 1	0	0.089	0.007	0.14	1.428	0.193		0.005	0	0.001
Port 4	0	0.024	0	0.056	3.359	0.355		0.004	0.001	0
Port 8	0	0.071	0.026	0.11	1.285	0.187		0.1	0.002	0.022
Sal 1	0	0.026	0.019	1.186	6.826	0.374		0.005	0.031	0.003
Hard 1	0	0.172	0.006	0.106	1.832	0.215		0.006	0	0
Hard 3	0	0.117	0.005	0.159	4.981	0.734		0.002	0.015	0.134
Jak 1	0	0.63	0.008	0.133	3.705	0.221		0.011	0.005	0
Kuil 1	0	0.06	0	0.105	2.67	0.142		0	0.035	0.008
Elim 1	0	0.051	0	0	2.54	0.246		0	0.09	0.036
Boes 5	0	0.11	0	0	5.561	0.355		0.004	0.043	0.007
Klip 5	0	0.11	0.021	0.085	3.129	0.22		0.008	0.019	0.019
Rooi 6	0.032	0.032	0	0.138	1.58	0.068		0.011	0.009	0.06
Rooi 7	0	0.14	0.011	0.11	1.065	0.105		0.002	0.097	0.054
Vol 3	0.031	0.195	0.01	0.187	5.4	0.433		0.005	0.127	0.153
Ou 1	0	0.062	0	0.191	0.66	0.092		0.037	0.01	0.133
Har 1	0	0.08	0	0	1.169	0.044	0.088	0	0.091	0.077
Har 2	0	0.261	0	0	3.713	0.131	0.046	0	0.026	0.012
Geel 3	0	0.07	0.066	0	12	0.106	0.073	0	0.562	0.008
El 1	0	0.109	0	0	5.303	0.293	0.011	0	0.034	0.007
El 4	0	0.126	0	0	1.932	0.056	0.056	0	0.046	0.023
Fon 2	0	0.162	0	0	5.318	0.132	0.08	0	0.085	0.014
PA 1	0.003	0.102	0	0	2.598	0.017	0.074	0	0.251	0.083
Guns 8	0.021	0.053	0	0	4.375	0.044	0.047	0	0.25	0.019
Brink 1	0	0.163	0.019	0	4.62	0.257	0.7	0	0.034	0
Brink 2	0	0.076	0	0	3.381	1.724	0.098	0.015	0.005	0.188

GROUNDWATER CHEMISTRY - TRACE ELEMENTS IN PARTS PER MILLION										
SITE	Al	Ba	Ni	P	Sr	B	U	Cu	Mn	Zn
Man 1	0	0.039	0	0	1.828	0.428	0.116	0.001	0.012	0
KK 1	0.001	0.053	0	0	2.799	0.053	0.078	0	0	0.099
Twee 3	0	0.028	0	0	2.034	0.168	0.1	0	0.014	0
MR 1	0.004	0.021	0	0	6.318	1.044	0.084	0	0.008	0
MR 2	0	0.019	0	0	6.654	0.671	0.045	0	0.011	0.003
MR 3	0	0.045	0	0	4.497	0.764	0.166	0	0.033	0.472
Ber 1	0.006	0.039	0	0	0.66	0.133	0.112	0.015	0.003	0.034
Bav 1	0	0.056	0.204	0	1.288	0.622	0.126	0.003	0.002	0.201
Bav 2	0	0.222	0	0	1.556	1.305	0.071	0	0	0
Pal 2	0.007	0.057	0	0	0.905	0.11	0.073	0	0	0.037
Swart 2	0	0.077	0	0	2.836	0.471	0.096	0	0.03	0
Dut 1	0.005	0.057	0	0	3.72	0.175	0.103	0	0.114	0.017
ROD 1	0.003	0.031	0	0	1.237	0.152	0.087	0.042	0	0.371
Vred 3	0	0.049	0	0.482	3.285	0.063	0	0.003	0	0.013
Font 1	0	0.033	0	0	1.071	0.125	0.162	0.001	0.001	0.009
Pan 2	0	0.071	0	0	3.842	0.859		0	0.036	0.018
Vyf 6	0	0.167	0.118	0	1.147	0.023	0.065	0	0	0.019
RK 1	0	0.143	0	0	1.626	0.179	0.07	0	0	0
Kuil 15	0	0.07	0.011	0.115	1.206	0.196		0.002	0.008	0.544
Mid 5	0	0.051	0.004	0.21	0.455	0.048		0	0.007	0.037
Jak 5	0	0.171	0.028	0.116	2.014	0.062		0.001	0.047	0.073
RD 1	1.262	0.009	0	0	0.101	0	0.01	0	0.018	0.233
RD 2	0	0.076	0.026	0	0.402	0.024	0.021	0	0	0.028
Pal 1	0.004	0.035	0	0	0.593	0.048	0.111	0	0.639	0.066
Hot 1	0	0.138	0	0	2.263	0.036	0	0.003	0.009	0
Kook 1	0	0.042	0	0.268	2.512	0.304		0.001	0.004	0.005
Vred 11	0	0.142	0.004	0.229	1.007	0.124		0.003	0.023	0.006
Sal 5	0	0.062	0.014	0.069	4.412	0.128		0.01	0.01	0.184
Kuil 6	0	0.074	0.014	0.123	1.584	0.125		0.002	0.004	0.046
Sut 1	0	0.046	0.011	0.373	1.403	1.306		0.008	0.008	0
Blyd 6	0	0.041	0.014	0.13	1.746	0.365		0.005	0.033	0

GROUNDWATER CHEMISTRY - TRACE ELEMENTS IN PARTS PER MILLION

SITE	Al	Ba	Ni	P	Sr	B	U	Cu	Mn	Zn
PA 2	0.009	0.051	0.229	0	1.84	0.082	0.124	0.001	0	0.045
PA 4	0.006	0.069	0.036	0	2.948	0.073	0.098	0	0.004	0.018
Uit 3	0	0.042	0	0	1.099	0.139	0.106	0	0	0.042
Sny 1	0.014	0.048	0.027	0	0.941	0.46	0.101	0.024	0.129	0.042
Sny 4	0	0.032	0.011	0	0.377	0.079	0.088	0	0	0.015
Haak 1	0.016	0.032	0	0	2.457	0.368	0.047	0	0.013	0.008
Stof 2	0	0.085	0	0	2.106	0.235	0.016	0	0.002	0.034
Stof 3	0	0.096	0	0	1.403	0.325	0.107	0	0	0.007
RW 1	0.004	0.045	0	0	1.348	0.22	0.092	0	0	0.025
Druip 1	0.014	0.039	0.026	0	1.009	0.516	0.078	0.008	0	0.041
Wil 1	0	0.039	0	0	1.828	0.428	0.088	0.001	0.012	0
Mar 6	0	0.119	0.132	0	1.718	0.116	0.092	0.008	0.024	0.037
Sal 2	0	0.027	0	0.51	2.015	0.097	0.049	0.002	0.023	0.016
Bron 3	0	0.054	0	0.049	1.109	0.511	0	0.006	0.002	0
Kuil 14	0	0.053	0	0.452	1.199	0.415	0.068	0	0.008	0
Vred 2	0	0.141	0.001	0.134	1.724	0.182		0.001	0.012	0.004
Vred 10	0	0.065	0.025	0.115	1.537	0.081		0.004	0.018	0.084
Vred 12	0	0.041	0.013	0.099	1.862	0.265		0.031	0.003	0.124
Kuil 7	0	0.071	0.029	0.113	1.923	0.259		0.016	0.09	0.088
Sut 2	0	0.13	0.015	0	2.314	0.258		0	0.004	0
Blyd 1	0	0.024	0.009	0.121	0.678	0.892		0.001	0.008	0
Welt 6	0	0.035	0.006	0.047	0.534	0.025		0.003	0.235	0.063
Welt 7	0	0.021	0	0.091	0.592	0.047		0	0.053	0.075
Geel 2	0	0.025	0.029	0	11.42	0.92	0.05	0	0.005	0.391
Hoek 1	0.012	0.16	0	0	4.215	0.145	0.091	0	0.18	0.024
Guns 2	0	0.136	0	0	3.635	0.144	0.084	0	0	0.016
Eland 6	0.002	0.066	0.024	0	0.847	0.052	0.115	0.035	0	0.486
Eland 7	0	0.037	0	0	0.735	0.08	0.105	0	0.065	0
Bas 1	0	0.007	0.074	0	0.227	0.016	0.069	0	0	0.037
SK 1	0	0.034	0	0	0.669	0.094	0.107	0.001	0.006	0.018
Sout 4	0	0.072	0.008	0.099	2.898	0.314		0.008	0	0.028

GROUNDWATER CHEMISTRY - TRACE ELEMENTS IN PARTS PER MILLION										
SITE	Al	Ba	Ni	P	Sr	B	U	Cu	Mn	Zn
Sout 2	0	0.071	0.012	0.11	3.349	0.295		0	0	0.034
Lang 3	0	0.057	0	0.552	0.978	0.297	0	0.003	0.053	0.004
Rhee 1	0	0.055	0	0.644	1.121	0.133	0	0.004	0.387	0.002
Heb 6	0	0.024	0	0.515	2.46	0.267	0	0.006	0.29	0
Bron 4	0	0.131	0.024	0.083	1.385	0.754		0.003	0.023	0.102
Jag 2	0	0.008	0.004	0.17	0.614	0.056		0.008	0	0.013
Heb 2	0	0.072	0	0.137	2.042	0.256		0	0.011	0.098
Vyf 2	0.157	0.032	0	0.129	0.325	0.043		0.018	0.009	3.367
Vyf 5	0	0.07	0	0.152	3.221	0.152		0	0.823	0
Bok 1	0	0.067	0	0	1.717	0.089	0.134	0	0.06	0.003
Twee 1	0.017	0.078	0	0	1.512	0.114	0.06	0.016	0.004	1.177
Twee 2	0.004	0.046	0	0	0.512	0.08	0.107	0.011	0	0.108
Twee 4	0.004	0.054	0	0	1.004	0.06	0.106	0.005	0	0.25
Eend 1	0.031	0.041	0.014	0	1.793	0.194	0.167	0	0.001	0.05
Swart 1	0.007	0.046	0	0	0.863	0.172	0.078	0.004	0	0.031

ISOTOPE DATA		
SITE	**δ^2H**	**$\delta^{18}O$**
KUIL 14	-34	-4.6
JAG 2	-38	-5.7
VRED 3	-35	-5.2
JAK 1	-36	-6
SUT 2	-34	-5.4
OU 1	-37	-5.8
ELAND 7	-31	-5
GUNS 8	-35	-5.4
HEB 6.1	-38	-5.5
HEB 6.6	-36	-5.4
PA 1	-39	-6.2
ELAND 6	-34	-4.7
SWART 3	-35	-5.1
SOUT 2	-34	-4.7
ELIM 1	-39	-6.3
MAR 6	-27	-3.6
KUIL 9	-29	-3.5
BRON 3	-37	-5.5
SAL 2	-41	-6.3
RHE 1	-36	-5.6
LANG 3	-40	-5.9
KLIP 12	-32	-5

APPENDIX IV

Saturation indices and log activities

GROUNDWATER CHEMISTRY -SATURATION INDICES

SITE	Magnesite	Aragonite	Calcite	Dolomite	Strontianite	$MnHPO_4$	Fluorite	Celestite	Anhydrite	Gypsum	Barite
Rhoog 1	-0.715	-0.288	-0.141	-0.497		0.741					0.26
Swart 3	-0.475	-0.198	-0.049	-0.174			-0.113				-0.095
Kuil 9	-0.232	-0.107	0.043	0.157		-0.582	-0.256				-0.278
Klip 12	-0.826	-0.037	0.111	-0.364	-0.919		-0.005				0.142
Brak 2	-0.972							-0.817			0.798
Brak 4	-0.374	-0.156	-0.005	-0.046		0.67		-0.683	-0.983	-0.639	0.701
Port 1	0.019	0.103	0.25	0.624							0.613
Port 4	-0.404	0.009	0.161	0.092	-0.753		0.211				0.099
Port 8	-0.412	0.219	0.374	0.027	-0.908	-0.657					0.547
Sal 1	0.008	0.182	0.334	0.674	0.631			-0.761		-0.929	0.278
Hard 1	-0.661				-0.822						0.704
Hard 3	-0.093	0.042	0.194	0.433	-0.912	-0.146		-0.881		-0.909	0.957
Jak 1	-0.858	-0.256	-0.105	-0.624	-0.897	-0.168					0.922
Kuil 1	0.195	0.014	0.164	0.313	-0.943	0.381					0.306
Elim 1	0.175	0.326	0.473	1.006	-0.75		-0.6				261
Boes 5	-0.048	0.335	0.481	0.794	-0.007		0.024				0.326
Klip 5	-0.41	0.22	0.368	0.312	-0.64	0.124	-0.223				0.535
Rooi 6	-0.345	-0.08	0.071	0.063		-0.162	-0.632				0.04
Rooi 7	-0.668	-0.272	-0.123	-0.442		0.995					0.596
Vol 3	-0.167	0.09	0.238	0.422		0.78	-0.923	-0.805	-0.882	-0.591	
Ou 1	-0.501	-0.381	-0.237	-0.37		0.096	-0.811				0.091
Har 1	-0.859	-0.284	-0.137	-0.639							0.375
Har 2	-0.53	0.064	0.21	0.041	-0.733						0.696
Geel 3	-0.67	0.011	0.161	-0.167	-0.912		-0.423	-0.733		-0.806	0.42
El 1		-0.322	-0.172				-0.573	-0.728		-0.706	1.043
El 4		-0.995	-0.846								0.012
Fon 2		-0.076	0.074	-0.659	-0.862		-0.224				
PA 1	-0.85	-0.161	-0.012	-0.514						-0.999	0.893
Guns 8	-0.504	-0.002	0.149	-0.016	-0.931		-0.594				0.439
Brink 1	-0.021	0.319	0.464	0.81	-0.71		-0.657				0.602

GROUNDWATER CHEMISTRY -SATURATION INDICES											
SITE	Magnesite	Aragonite	Calcite	Dolomite	Strontianite	$MnHPO_4$	Fluorite	Celestite	Anhydrite	Gypsum	Barite
Brink 2	0.138	0.588	0.737		-0.458		0.159				0.384
Man 1	-0.045	0.201	0.348	0.662			-0.715				0.387
KK 1	-0.442	0.031	0.179	0.09			-0.605				0.08
Twee 3	-0.321	-0.033	0.115	0.15							0.113
MR 1		-0.07	0.076	-0.574	-0.769		-0.294	-0.816			0.06
MR 2	-0.829	0.025	0.172	-0.3	-0.625		-0.175	-0.79			0.042
MR 3	0.4	0.43	0.575		-0.546		0.008	-0.803		-0.861	0.591
Ber 1	-0.211	0.16	0.306	0.459			-0.654				-0.288
Bav 1	-0.205	0.124	0.269	0.429			-0.394				0.124
Bav 2	-0.624	-0.367	-0.22	-0.488	-0.908		-0.429				0.693
Pal 2	-0.48	0.048	0.195	0.071			-0.405				-0.256
Swart 2	0.003	0.474	0.621	0.981	-0.461		-0.123				0.287
Dut 1	-0.658	-0.097	0.052	-0.26						-0.961	0.526
ROD 1	-0.445	-0.025	0.122	0.033			-0.631				0.034
Vred 3	-0.445	-0.116	0.033	-0.063	-0.91		0.029				-0.152
Font 1											
Pan 2	-0.258	0.217	0.367	0.45	-0.631		0.479				0.692
Vyf 6	-0.464	-0.14	0.007	-0.099			-0.838				0.318
RK 1	-0.042	0.232	0.379	0.697	-0.844		-0.753				0.419
Kuil 15		-0.256	-0.107	-0.422		-0.117	-0.267				-0.034
Mid 5	-0.029	0.289	0.436	0.767		0.289					-0.219
Jak 5	-0.839	-0.08	0.072	-0.433		0.681					0.746
RD 1											
RD 2			-0.921								-0.299
Pal 1	-0.456	-0.059	0.087	-0.01			-0.527				-0.937
Hot 1	-0.916	-0.087	0.061	-0.5							-0.16
Kook 1	-0.39	0.083	0.234	0.181	-0.898	-0.102					0.425
Vred 11	-0.736	-0.072	0.078	-0.313		0.782					0.316

GROUNDWATER CHEMISTRY -SATURATION INDICES											
SITE	Magnesite	Aragonite	Calcite	Dolomite	Strontianite	$MnHPO_4$	Fluorite	Celestite	Anhydrite	Gypsum	Barite
Sal 5	0.103	0.454	0.605		-0.142	-0.213					0.189
Kuil 6	-0.136	0.006	0.155	0.365		-0.459	-0.025				0.487
Sut 1	-0.617	0.232	0.381	0.111	-0.564	0.595	0.667				0.623
Blyd 6	0.241	0.291	0.439		-0.788	0.457	0.015				0.238
PA 2	-0.944	-0.155	-0.005	-0.602			-0.745				
PA 4	-0.742	-0.177	-0.03	-0.415	-0.978						0.198
Uit 3	-0.448	-0.155	-0.008	-0.097			-0.421				-0.009
Sny 1	-0.288	-0.107	0.041	0.167			-0.69				0.442
Sny 4	-0.35	-0.178	-0.031	-0.025							-0.169
Haak 1	-0.765	0.019	0.168	-0.248			-0.62				0.256
Stof 2	-0.44	-0.032	0.116	0.031							0.513
Stof 3	-0.456	-0.084	0.063	-0.038							0.628
RW 1	-0.196	-0.045	0.102	0.266			-0.375				0.215
Druip 1	-0.391	-0.039	0.11	-0.345				0.067			0.069
Wil 1	-0.061	0.208	0.355	0.65							-0.338
Mar 6	-0.077	0.284	0.431	0.709							0.472
Sal 2	-0.254	-0.083	0.066	0.16		0.879	0.327				-0.226
Bron 3	-0.633	-0.219	-0.071	-0.35		-0.994	-0.6				0.181
Kuil 14	-0.463	-0.274	-0.125	-0.24		0.358	-0.288				0.269
Vred 2		-0.563	-0.414			-0.021					0.479
Vred 10	-0.652	-0.039	0.12	-0.242	-0.932	0.399					0.204
Vred 12	0.343	0.77	0.919		-0.18	-0.557					-0.087
Kuil 7	-0.436	-0.215	-0.066	-0.156		0.751	0.014				0.246
Sut 2	-0.32	0.148	0.298	0.32	-0.603						0.659
Blyd 1	-0.037	0.19	0.335	0.665	-0.627	0.101	0.37				
Welt 6						0.897					-0.074
Welt 7	-0.886	-0.553	-0.404	-0.939		0.618					-0.669
Geel 2		0.048	0.196	-0.498	-0.673		0.354	-0.341	-0.918	-0.629	0.455

GROUNDWATER CHEMISTRY -SATURATION INDICES

SITE	Magnesite	Aragonite	Calcite	Dolomite	Strontianite	$MnHPO_4$	Fluorite	Celestite	Anhydrite	Gypsum	Barite
Hoek 1	-0.964	-0.133	0.015	-0.596							0.72
Guns 2		-0.144	0.006	-1.008	-0.888		-0.693				0.631
Eland 6	-0.041	0.217	0.363	0.684							-0.19
Eland 7	-0.126	0.07	0.218	0.445			-0.891				-0.201
Bas 1	-0.588	-0.439	-0.292	-0.522							
SK 1	-0.546	-0.101	0.045	-0.139			-0.779				-0.138
Sout 4	-0.176	0.005	0.153	0.331	-0.938						0.496
Sout 2	-0.249	0.009	0.156	0.266	-0.796						0.36
Lang 3	-0.586	-0.294	-0.144	-0.386			-0.342				0.309
Rhee 1	-0.844	-0.297	-0.148	-0.643			-0.825				0.098
Heb 6	-0.537	-0.262	-0.111	-0.308			-0.52				0.072
Bron 4	-0.069	0.15	0.298	0.583		0.109	-0.259				0.55
Jag 2	-0.269	0.059	0.206	0.293							
Heb 2	0.015	0.235	0.383	0.748	-0.841	-0.043	-0.316				0.416
Vyf 2						-0.008					-0.767
Vyf 5	-0.919	-0.452	-0.302	-0.875				-0.83	-0.838	-0.531	
Bok 1	-0.243	-0.018	0.132	0.236			-0.487				0.587
Twee 1	-0.196	0.083	0.231	0.388			-0.366				0.253
Twee 2	-0.337	-0.178	-0.032	-0.007			-0.768				-0.19
Twee 4	-0.59	-0.301	-0.153	-0.388			-0.351				0.115
Eend 1	0.19	0.338	0.483		-0.878		-0.3				0.06
Swart 1	-0.296	-0.047	0.101	0.159			-0.819				0.059

GROUNDWATER CHEMISTRY - LOG ACTIVITIES

SITE	<Ca>	<Sr>	<CO3>	<F2>	<Mg>	<Ba>	<SO4>	SITE	<Ca>	<Sr>	<CO3>	<F2>	<Mg>	<Ba>	<SO4>
Rhoog 1	-2.77	-4.764	-5.829	-9.334	-3.064	-6.836	-2.943	Pal 1	-3.018	-5.358	-5.353	-8.516	-3.281	-6.756	-4.221
Swart 3	-2.988	-5.358	-5.506	-8.164	-3.105	-6.971	-3.205	Hot 1	-2.882	-4.772	-5.511	-9.46	-3.57	-6.16	-4.053
Kuil 9	-3.102	-5.292	-5.296	-8.206	-3.057	-6.975	-3.4	Kook 1	-2.902	-4.877	-5.295		-3.181	-6.756	-2.95
Klip 12	-3.009	-4.863	-5.326	-8.032	-3.64	-6.385	-3.551	Vred 11	-3.028	-5.136	-5.334		-3.517	-6.145	-3.641
Brak 2	-7.14	-4.276	-6.327		-2.728	-6.204	-3.132	Sal 5	-2.959	-4.553	-4.865		-3.109	-6.549	-3.403
Brak 4	-2.263	-4.291	-6.168		-2.274	-6.464	-2.985	Kuil 6	-2.994	-5.039	-5.292	-8.084	-2.964	-6.489	-3.121
Port 1	-2.844	-5.146	-5.357		-2.78	-6.451	-2.997	Sut 1	-3.368	-5.143	-4.692	-7.012	-4.05	-6.691	-2.779
Port 4	-2.984	-4.746	-5.283	-7.892	-3.195	-7.006	-3.037	Blyd 6	-2.982	-5.03	-5.027	-8.034	-2.879	-6.774	-3.059
Port 8	-2.931	-5.092	-5.105		-3.304	-6.481	-3.192	PA 2	-2.801	-4.88	-5.647	-8.938	-3.422	-6.617	-5.419
Sal 1	-2.732	-4.548	-5.36		-2.697	-7.067	-2.807	PA 4	-2.946	-4.706	-5.541	-9.282	-3.376	-6.479	-3.368
Hard 1		-4.874	-5.254		-3.337	-6.062	-3.519	Uit 3	-3.018	-5.163	-5.448	-8.41	-3.178	-6.715	-3.334
Hard 3	-2.749	-4.705	-5.483		-2.678	-6.422	-2.769	Sny 1	-2.953	-5.346	-5.455	-8.766	-2.923	-6.725	-2.9
Jak 1		-4.592	-5.579		-3.37	-5.53	-3.674	Sny 4	-2.988	-5.617	-5.496	-9.51	-3.017	-6.829	-3.394
Kuil 1	-2.869	-4.809	-5.405	-8.45	-2.902	-6.592	-3.208	Haak 1	-2.77	-4.852	-5.508	-8.89	-3.394	-6.839	-2.986
Elim 1	-2.841	-4.876	-5.143	-8.77	-2.856	-6.686	-3.096	Stof 2	-2.687	-4.945	-5.647	-9.358	-2.947	-6.458	-3.091
Boes 5	-3.176	-4.473	-4.804	-7.8	-3.431	-6.314	-3.391	Stof 3	-2.684	-5.146	-5.705	-9.37	-2.91	-6.419	-3.012
Klip 5	-2.903	-4.73	-5.179	-8.346	-3.384	-6.311	-3.218	RW 1	-2.923	-5.136	-5.435	-8.458	-2.941	-6.727	-3.096
Rooi 6	-2.753	-5.051	-5.607	-8.958	-2.823	-6.885	-3.208	Druip 1	-2.898	-5.222	-5.436	-8.49	-3.087	-6.765	-3.252
Rooi 7	-3.047	-5.147	-5.52	-9.122	-3.282	-6.166	-3.321	Wil 1	-2.779	-4.958	-5.319	-9.198	-2.902	-6.787	-3.608
Vol 3	-2.479	-4.673	-5.729	-9.48	-2.577	-6.191	-2.717	Mar 6	-2.748	-5.008	-5.274	-9.35	-2.966	-6.303	-3.28
Ou 1	-2.95	-5.394	-5.762	-8.832	-2.966	-6.566	-3.335	Sal 2	-3.01	-4.908	-5.367	-7.71	-3.014	-6.921	-3.397
Har 1	-2.929	-5.115	-5.663	-9.724	-3.363	-6.412	-3.263	Bron 3	-3.098	-5.152	-5.423	-8.53	-3.362	-6.605	-3.279
Har 2	-2.877	-4.625	-5.377	-9.14	-3.347	-5.925	-3.402	Kuil 14	-3.13	-5.167	-5.436	-8.206	-3.151	-6.645	-3.179
Geel 3	-2.351	-4.261	-5.924	-9.136	-2.849	-6.633	-3.062	Vred 2	-2.923	-4.941	-5.93		-3.266	-6.179	-3.444
El 1	-2.599	-4.602	-6.013	-9.028	-3.435	-6.344	-2.713	Vred 10	-2.993	-4.953	-5.284		-3.3	-6.491	-3.589
El 4	-2.837	-4.861	-6.45	-9.73	-3.3	-6.221	-3.861	Vred 12	-3.002	-4.932	-4.52		-3.259	-6.73	-3.453
Fon 2	-2.67	-4.441	-5.694	-8.614	-3.494	-6.14		Kuil 7	-3.008	-4.932	-5.498	-8.028	-3.059	-6.498	-3.353
PA 1	-2.752	-4.86	-5.702	-9.752	-3.274	-6.345	-2.853	Sut 2	-3.074	-4.813	-5.063	-8.866	-3.359	-6.196	-3.259
Guns 8	-2.725	-4.646	-5.558	-8.942	-3.037	-6.68	-3.008	Blyd 1	-3.574	-5.332	-4.564	-7.03	-3.694	-6.941	-4.975
Brink 1	-2.65	-4.622	-5.357	-8.984	-2.881	-6.205	-3.195	Welt 6	-3.213	-5.398	-6.399	-9.448	-3.401	-6.735	-3.442

GROUNDWATER CHEMISTRY - LOG ACTIVITIES

SITE	<Ca>	<Sr>	<CO3>	<F2>	<Mg>	<Ba>	<SO4>	SITE	<Ca>	<Sr>	<CO3>	<F2>	<Mg>	<Ba>	<SO4>
Brink 2	-2.725	-4.744	-4.985	-8.152	-3.018	-6.521	-3.172	Welt 7	-3.093	-5.358	-5.757	-9.272	-3.269	-6.973	-3.773
Man 1	-2.866	-5.077	-5.245	-8.856	-2.979	-6.822	-2.831	Geel 2	-2.632	-4.325	-5.618	-8.05	-3.568	-7.02	-2.601
KK 1	-2.7	-4.779	-5.57	-8.932	-3.022	-6.648	-3.339	Hoek 1	-2.764	-4.601	-5.671	-9.302	-3.446	-6.147	-3.198
Twee 3	-2.794	-4.975	-5.545		-2.939	-6.94	-3.002	Guns 2	-2.897	-4.629	-5.532	-8.864	-3.922	-6.195	-3.293
MR 1	-2.82	-4.471	-5.567	-8.47	-3.639	-7.039	-2.925	Eland 6	-2.978	-5.239	-5.124	-9.302	-3.115	-6.501	-3.71
MR 2	-2.841	-4.451	-5.443	-8.346	-3.558	-7.082	-2.921	Eland 7	-3.025	-5.314	-5.207	-8.896	-3.069	-6.756	-3.512
MR 3	-2.865	-4.785	-5.031	-8.104	-2.785	-6.814	-2.597	Bas 1	-3.078	-5.781	-5.671	-10.088	-3.092	-7.458	-3.927
Ber 1	-2.943	-5.363	-5.217	-8.698	-3.196	-6.739	-3.564	SK 1	-3.006	-5.344	-5.412	-8.77	-3.326	-6.778	-3.385
Bav 1	-2.872	-5.137	-5.328	-8.506	-3.085	-6.627	-3.259	Sout 4	-2.909	-4.817	-5.39		-2.946	-6.531	-3.03
Bav 2	-3.496	-4.999	-5.178	-7.95	-3.61	-5.987	-3.373	Sout 2	-2.955	-4.718	-5.347		-3.078	-6.513	-3.17
Pal 2	-2.974	-5.195	-5.285	-8.448	-3.361	-6.553	-3.754	Lang 3	-2.977	-5.239	-5.605	-8.422	-3.093	-6.601	-3.195
Swart 2	-2.882	-4.779	-4.952	-8.256	-3.213	-6.48	-3.283	Rhee 1	-3.003	-5.117	-5.587	-8.868	-3.384	-6.571	-3.42
Dut 1	-2.641	-4.735	-5.746		-3.028	-6.649	-2.926	Heb 6	-2.819	-4.918	-5.727	-8.77	-2.908	-7.041	-3.007
ROD 1	-2.832	-5.154	-5.5	-8.816	-3.111	-6.872	-3.146	Bron 4	-2.895	-5.099	-5.257	-8.39	-2.964	-6.26	-3.255
Vred 3	-2.904	-4.673	-5.508	-8.108	-3.072	-6.65	-3.586	Jag 2	-3.034	-5.35	-5.213	-9.474	-3.219	-7.399	-3.721
Font 1								Heb 2	-2.904	-4.953	-5.158	-8.452	-2.963	-6.525	-3.141
Pan 2	-2.87	-4.707	-5.197	-7.718	-3.16	-6.537	-2.889	Vyf 2	-3.34	-5.556	-6.653	-9.722	-3.57	-6.745	-4.083
Vyf 6	-2.816	-5.133	-5.632	-9.038	-3	-6.127	-3.605	Vyf 5	-2.619	-4.899	-6.123	-9.818	-2.915	-6.567	-2.518
RK 1	-2.953	-4.984	-5.129	-8.802	-3.098	-6.184	-3.43	Bok 1	-2.759	-5.071	-5.55	-8.778	-2.816	-6.578	-2.93
Kuil 15	-3.044	-5.076	-5.506	-8.27	-3.283	-6.468	-3.656	Twee 1	-2.893	-5.04	-5.327	-8.5	-3.023	-6.465	-3.346
Mid 5	-3.142	-5.471	-4.88		-3.327	-6.578	-3.681	Twee 2	-3.061	-5.464	-5.435	-8.702	-3.096	-6.662	-3.552
Jak 5	-2.861	-4.871	-5.495		-3.42	-6.081	-3.316	Twee 4	-2.949	-5.208	-5.657	-8.424	-3.093	-6.616	-3.328
RD 1	-3.626	-6.035	-7.066	-10.826	-3.729	-7.274	-5.091	Eend 1	-2.863	-5.024	-5.124	-8.416	-2.9	-6.782	-3.161
RD 2	-3.131	-5.504	-6.244	-9.7	-3.439	-6.399	-3.885	Swart 1	-2.918	-5.292	-5.433	-8.922	-3.022	-6.699	-3.301

APPENDIX V

Data for the borehole (HEB6) pumped over a four hour period

CHEMISTRY DATA FOR HEB6

	TIME (min)	pH	EC (mS/m)	TEMP. (^oC)	Eh (mV)	Cl	HCO_3	SO_4	NO_3	F	P	K	Ca	Mg	Na	Sr	Ba	Cu	Ni	U	Zn	Mn	B
HEB61	1	6.869	270	15.9	7.1	511.6	494.5	232.3	0	1	0.515	5.652	131.8	62.67	369.4	2.46	0	0	0	0	0	0.29	0.3
HEB62	20	6.48	316	16.5	27.1	599.8	487.5	254.6	0	1.5	0.264	5.654	117.1	62.17	463.4	3.205	0	0	0	0	0	0.17	0.3
HEB63	40	6.401	321	16.9	30.5	599.8	501	250.3	0	1.7	0	5.315	105.6	58.36	500.1	3.193	0	0	0	0	0	0.14	0.4
HEB64	60	6.66	325	16.8	19.8	617.5	504	247.1	0	1.8	0.518	4.884	99.54	56.35	500.1	3.204	0	0	0	0	0	0.13	0.4
HEB65	80	6.686	333	16.8	15.5	620	507.38	248.5	0	1.8	0.342	5.431	95.58	55.38	521.7	3.215	0.34	0	0	0	0	0.12	0.4
HEB66	200	7.164	332	18.3	-10.1	652.7	514.6	245.4	0	2.1	0.213	5.626	88.76	52.81	563.9	3.236	0.35	0	0	0	0	0.1	0.4
HEB67	220	7.264	328	18.2	-15.7																		
HEB68	240	7.248	330	17.9	-14	652.7	497.7	241.3	0	2.2	0.526	4.953	83.49	50.2	551.5	3.157	0	0	0	0	0	0.1	0.4

All values in ppm, unless otherwise indicated.