

# Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa

S. Adams<sup>a,\*</sup>, R. Titus<sup>a</sup>, K. Pietersen<sup>b</sup>, G. Tredoux<sup>c</sup>, C. Harris<sup>d</sup>

<sup>a</sup>Department of Earth Sciences, P.O. Box XI7, University of the Western Cape, Bellville, 7535, South Africa

<sup>b</sup>Water Research Commission, P.O. Box 824, Pretoria, 0001, South Africa

<sup>c</sup>Cape Water Programme, CSIR, P.O. Box 320, Stellenbosch, 7599, South Africa

<sup>d</sup>Geological Sciences, University of Cape Town, Rondebosch, 7700, South Africa

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## Abstract

The Western Karoo depends entirely on groundwater for domestic and agricultural use. An understanding of the chemical evolution of the groundwater provides insight into the interaction of water with the environment and contributes to better resource management.

Descriptive statistics, correlation matrices and factor analysis, together with stable isotope data were used to gain an understanding of the hydrochemical processes of the groundwaters in the fractured rocks around Sutherland in the Western Karoo. The main processes influencing the groundwater chemistry are salinisation, mineral precipitation and dissolution, cation exchange and human activity. The stable isotope data indicate that the infiltration of evaporated water is partly responsible for the occurrence of saline subsurface waters. The ionic, oxygen and hydrogen stable isotope composition of the groundwaters suggests that the effects of localised topography are one of the overriding factors controlling the groundwater chemistry. In higher lying areas,  $\text{Ca}(\text{HCO}_3)_2$  type waters are prevalent, while in topographical flat areas NaCl type waters dominate. In areas where water collects close to or at the surface, saline soils are formed. From these areas salts are leached to the subsurface, during significant recharge periods. These findings are important in that they contribute to the identification of suitable locations for developing groundwater resources that could yield a relatively better quality water. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

As a resource, 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. Understanding the groundwater characteristics is crucial for

groundwater management in the study area. A study was conducted around the town of Sutherland and covers an area of approximately 3000 km<sup>2</sup> (Fig. 1). Undulating hills characterise the landscape. The hills are very often made up of doleritic intrusions.

Groundwater is drawn from the Permian sandstones and mudstones as well as from the contacts with the Jurassic dolerite dykes and sills in the Sutherland region. The occurrence of groundwater is mainly associated with fracture and joint systems. Due to the intrusive rocks in the area (dolerites, carbonatites

\* Corresponding author. Tel.: +27-21-959-1317; fax: +27-21-959-1317.

E-mail address: shadams@uwc.ac.za (S. Adams).

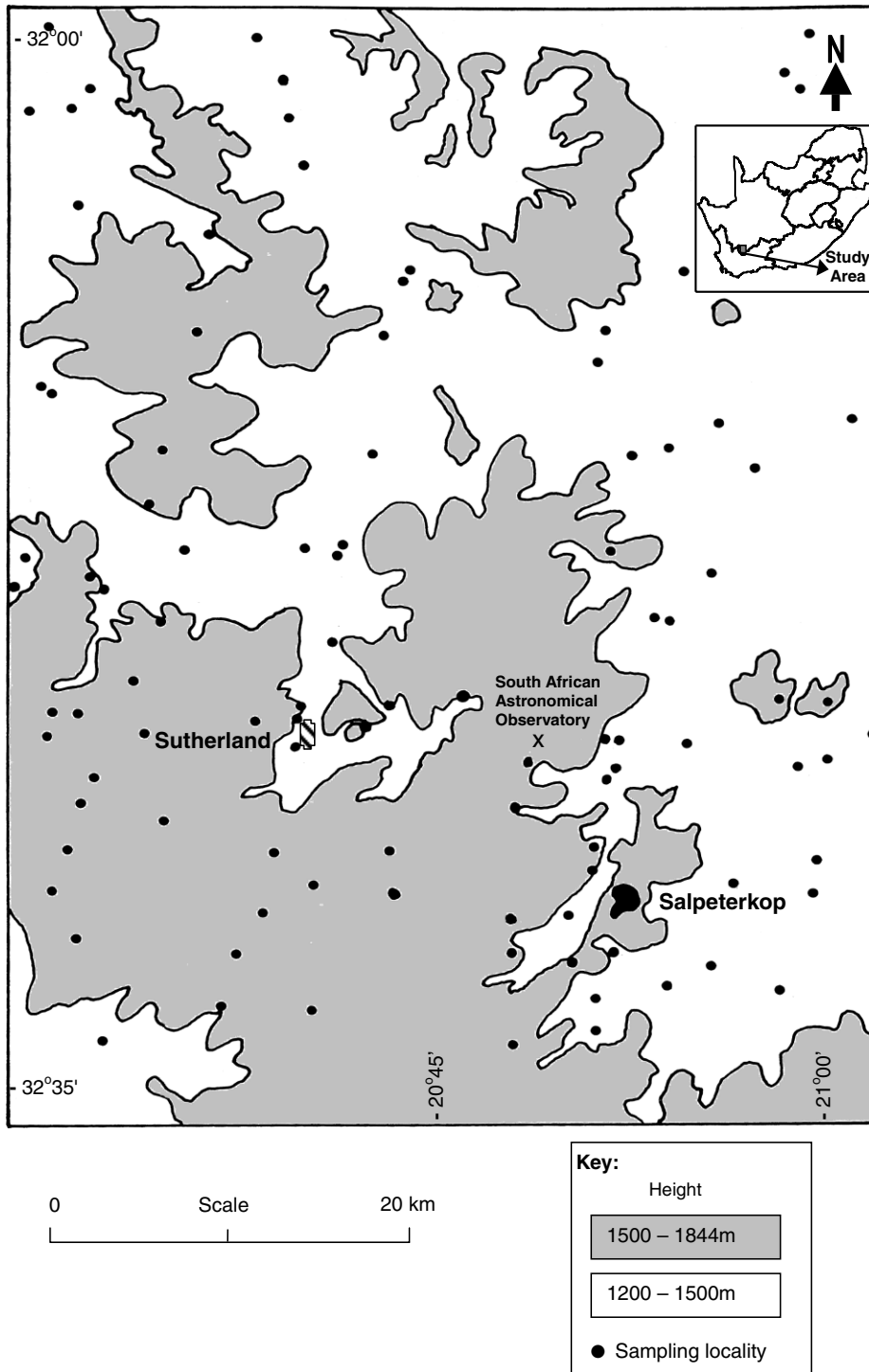


Fig. 1. Locality map of the study area.

Table 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	Stormberg <sup>a</sup>		
Triassic		Tarkastad <sup>a</sup>	
225 Ma	Beaufort (3000 m)		
Permian		Adelaide	Teekloof Abrahamskraal
Permian	Ecca (1800 m)		Waterford <sup>b</sup> Koedoesberg <sup>b</sup> Kookfontein <sup>b</sup> Skoorsteenberg <sup>b</sup> Tierberg Whitehill (not exposed)
270 Ma–Carboniferous	Dwyka (600 m)		Not exposed in study area

<sup>a</sup> Do not occur in the study area.

<sup>b</sup> Not yet approved.

and melilite basalts) and the major joints associated with the Cape Orogeny, the formations of the area have been highly fractured, making these formations good aquifers as a result of secondary permeability. However, detailed geohydrological information such as borehole logs, water strikes and detailed mineralogy are lacking for the study area.

The Western Karoo region is semi-arid with mean annual rainfall of 300–400 mm and evaporation rates of 1800–2000 mm per annum (Midgley et al., 1994). The average annual rainfall decreases westwards from approximately 500 mm in the east to less than 100 mm over the north-western areas. With the exception of the south-western parts, the major part of the Western Karoo receives mainly summer rain, from October to March (Venter et al., 1986). Daily and seasonal temperature fluctuations in the Karoo are large, with a range of 25°C between day and night temperatures not uncommon. The rivers that drain the study area are non-perennial in nature. These rivers only flow during periods of peak rainfall. Farmers generally dam these non-perennial rivers for irrigation and stock watering, while communities rely mainly on groundwater of variable quality for domestic supplies.

A research project was undertaken with the objective to establish, interpret and map the chemical composition of the groundwater of the area surrounding the

town of Sutherland (Fig. 1). As part of the study the hydrogeological and geomorphological conditions, which influence the chemical composition of the groundwater, were determined.

## 2. Geological framework

The main Karoo Basin covers an area of approximately 500 000 km<sup>2</sup> and basin fill took place from the late Carboniferous (280 Ma) to early Jurassic (100 Ma) (Visser et al., 1980). The Karoo sequence in the western half of the basin has a 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 sedimentary rocks of the Beaufort Group sediments follow the Ecca Group conformably (Table 1).

The sedimentary rocks are sandstones, shales, siltstones and mudstones belonging to the Beaufort Group (Adelaide Subgroup). Theron (1983) estimated 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. The Teekloof Formation is similar to the underlying Abrahamskraal Formation, except for the absence of limestone bands and chert layers (Theron, 1983). The sediments were intruded mainly by east–west

Table 2

Univariate statistical overview of the data set (rain and groundwater samples). All values in mg/l unless otherwise indicated. N.D. = Not determined. Std. dev. = Standard deviation. Sum = summation

	Rain ( <i>n</i> = 2) mean	Groundwater ( <i>n</i> = 108)				
		Mean	Median	Min.	Max.	Std. dev.
pH	5.2	7.3	7.3	6.3	8.5	0.3
EC (mS/m)	2	159	133	41	986	120
Temp. (°C)	12.8	18.6	19.2	5.9	24.1	3.0
Eh (mV)	N.D.	-15.3	-15.7	-71.0	37.9	17.5
<i>p</i> CO <sub>2</sub> (atm)	N.D.	0.02	0.01	0.000	0.1	0.01
Alkalinity	0.6	275	263	85	550	106
TDS (sum)	17	1053	940	132	5469	691
HCO <sub>3</sub>	8.7	312.8	311.5	55.6	563.6	112.1
K	0.2	2.7	2.0	0.5	18.2	2.6
F	<0.1	1.3	1	0.2	6.8	1.1
Cl	6.1	268.6	176.9	25.9	2923	348.5
Ca	0.3	107.2	89.7	11.8	633	79.9
SO <sub>4</sub>	0.6	147.8	100.0	<0.001	738.5	147.9
NO <sub>3</sub>	<0.1	4.7	0.2	<0.1	37.2	7.5
Mg	0.2	40.0	32.1	4.2	351.2	40.4
Na	0.2	159.4	131.3	14.1	807.4	133.2
Sr	0.01	2.5	1.8	0.1	14.2	2.4
Al	<0.001	0.02	<0.001	<0.001	1.3	0.1
Ba	0.002	0.1	0.1	0.01	0.6	0.1
Ni	0.02	0.01	<0.001	<0.001	0.2	0.04
P	0.1	0.1	<0.001	<0.001	1.2	0.2
B	0.003	0.3	0.2	<0.001	1.7	0.3
U	<0.001	0.1	0.1	<0.001	0.7	0.1
Cu	0.004	0.01	0.001	<0.001	0.1	0.01
Mn	<0.001	0.1	0.01	<0.001	0.8	0.1
Zn	<0.001	0.1	0.02	<0.001	3.4	0.4

trending basaltic dolerite dykes as well as sills during the Jurassic, which exploited fractures in the sedimentary rocks. During the Cretaceous the carbonatites and associated intrusions of the Salpeterkop Carbonatite complex intruded the geological formations.

### 3. Sampling and analytical procedures

A total of 110 boreholes were sampled for chemical analyses, each sample being analysed for the parameters listed in Table 2. Parameters that were measured and recorded at the time of sampling were alkalinity, electrical conductivity (EC), pH, temperature and redox potential (Eh). Alkalinity was measured using a Hach® field titration kit. The EC, pH, temperature and Eh was measured using portable Orion EC and pH meters. Water was only taken from

boreholes that were pumping for a significant amount of time. Samples were filtered in the field with a hand-held syringe using 0.45 µm membrane filters. Samples were collected in three new 250 ml polyethylene bottles. All sampling bottles were washed with de-ionised water and again with filtered sample water. Twenty-two localities were chosen for oxygen and hydrogen isotope analysis. Unfiltered samples were collected for isotope analyses.

The Agricultural Research Council's Infruitec laboratories performed major and minor ion analyses using a Varian Vista ICP Atomic Emission Spectrometer, except for nitrate and fluoride which were analysed at the laboratories of the Council for Scientific and Industrial Research (CSIR) using the cadmium reduction column method for nitrate and a specific ion electrode for fluoride. Two samples had ionic balance errors above 10% and were removed

Table 3  
Summary of saturation indices

Phase	n	Saturation Index			
		Maximum	Minimum	Mean	Standard deviation
Fluorite	86	0.67	-3.42	-0.65	0.64
Strontianite	106	0.63	-3.83	-1.16	0.56
Gypsum	102	-0.53	-7.02	-1.73	0.89
Calcite	106	0.92	-5.04	0.02	0.64
Barite	106	1.17	-2.30	0.17	0.57

from the data set. The Statistica (Statsoft) computer program was used to perform all statistical analysis. The extent of mineral saturation and  $p\text{CO}_2$  of all sampled water were determined using the NETPATH software package, through a WATEQF subroutine (Plummer et al., 1992). The saturation indices (SI) are expressed as  $\text{SI} = \log \text{IAP/KT}$ . The stable isotope analyses were performed at the Geochemistry Department of the University of Cape Town. The isotope ratios of  $\text{CO}_2$  and  $\text{H}_2$  were measured using a Finnegan MAT252 mass spectrometer. The results are reported as  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , where  $\delta = ((R_{\text{sample}}/R_{\text{standard}}) - 1) \times 1000$ . The standards V-SMOW and SLAP were analysed to determine the degree of compression of raw data and the equations of Coplen (1993) were used to convert to the SMOW scale (Harris et al., 1999). Drifts in reference gases were corrected by analysing an internal standard (CTMP), calibrated against V-SMOW and SLAP, with each batch of samples (Harris et al., 1999).

## 4. Groundwater chemistry

### 4.1. Descriptive statistics

Table 2 presents a univariate overview of the hydrochemical data of the study area. The concentrations of the chemical constituents in the groundwater are significantly higher than the rainwater. This is indicative of the dissolution of salts and other processes modifying the rainwater chemical composition during infiltration into the subsurface. The pH of the groundwater ranges between 6.3 and 8.5, an indication that the dissolved carbonates are predominantly in the  $\text{HCO}_3$  form. The higher partial

pressure of carbon dioxide ( $p\text{CO}_2$ ) in the infiltrating water compared to the precipitation  $p\text{CO}_2$  of  $10^{-3.5}$  atm suggests that the water has gained  $\text{CO}_2$  from root respiration and the decay of soil organic matter. Subsequently, an increase in  $p\text{CO}_2$  causes a drop in pH. The chemical composition of the groundwater varies over a wide range and this (see Table 2) indicates that the groundwater in the study area is not uniform but differs considerably, both in salinity and ionic composition.

The processes of dissolution, precipitation and cation exchange are actively taking place within the groundwater system. The saturation of groundwater with respect to fluorite, strontianite, gypsum, calcite and barite are summarised in Table 3. The mineral phases fluorite, strontianite and gypsum are undersaturated in the groundwaters. It is postulated that mineral phases that are undersaturated ( $\text{SI} \leq -0.1$ ) will tend to dissolve and mineral phases that are oversaturated ( $\text{SI} \geq 0.1$ ) will precipitate these mineral phases out of solution. Calcite and barite are distributed around saturation/equilibrium (i.e. oversaturated to undersaturated). Equilibrium is taken to be between  $\text{SI} = -0.1$  to  $0.1$ . An error of  $\pm 0.05$  pH units leads to an uncertainty of  $\pm 0.05$  units in the SI of minerals and in view of the uncertainties in the Ca, Mg and  $\text{HCO}_3$  analyses, the total uncertainties are of the order of  $\pm 0.1$  units of SI (Langmuir, 1971). The dissolution of minerals and the subsequent exchange between cations leads to the precipitation of minerals.

### 4.2. Correlation matrices

Pearson's correlation matrices (Swan and Sandilands, 1995) were used to find relationships between two or more variables. Only correlations with  $r > 0.4$

Table 4

Pearson's correlation matrices for data showing marked correlations at a significance level of  $<0.05$ . All values in mg/l unless otherwise indicated

	pH	EC	Sr	B	Mn	F	Cl	Ca	SO <sub>4</sub>	Mg	Na	HCO <sub>3</sub>	K	Eh	pCO <sub>2</sub>
pH	1														
EC <sup>a</sup>		1													
Sr		0.64	1												
B	0.40			1											
Mn					1										
F	0.64			0.59		1									
Cl		0.94	0.75				1								
Ca		0.81	0.81		0.40		0.87	1							
SO <sub>4</sub>		0.59	0.55				0.54	0.65	1						
Mg		0.88	0.52				0.89	0.81	0.55	1					
Na		0.83	0.67	0.50		0.47	0.82	0.59	0.63	0.73	1				
HCO <sub>3</sub>	0.45											1			
K											0.54		1		
Eh <sup>b</sup>	-0.91					-0.59								1	
pCO <sub>2</sub> <sup>c</sup>	-0.77											0.45		0.70	1

<sup>a</sup> In mS/m.

<sup>b</sup> In mV.

<sup>c</sup> In atm.

are shown (Table 4). Samples showing  $r > 0.7$  are considered to be strongly correlated whereas  $r > 0.5$ – $0.7$  shows moderate correlation at a significance level ( $p$ ) of  $<0.05$ .

Strong correlations exist among the major elements, Na, Ca, Mg and Cl, and EC ( $r > 0.7$ ) (Table 4). These relationships clearly identify the main elements contributing to the groundwater salinity and their tendency to follow a similar trend (e.g. due to concentration by evaporation). Moderate correlations ( $r > 0.5$ – $0.7$ ) between SO<sub>4</sub> and Sr with EC indicate that these ions tend to increase in concentration as the salinity of the water increases. The salinisation of the groundwater would be expected to result from the ionic concentrations increasing due to both evaporation of recharge water and to the effects of interactions between the groundwater and the geological formations.

The contributions of evaporitic salts are shown by the positive correlations between CaSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub> and SrSO<sub>4</sub>. The most important evaporite present is CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum). Gypsum deposits have been observed in the field where gypsum has been precipitated on fracture walls. Cole and Vorster (1999) have found gypsum deposits to the west of the study area in the Tierberg Formation (Ecca Group).

The oxidation of in situ pyrite and the reaction of sulphuric acid with carbonate under an evaporative condition were identified as the processes operative in the formation of the gypsum deposits (Cole and Vorster, 1999).

The major exchangeable ions Na–Ca, Na–Mg, Sr–Ca, Sr–Mg, Sr–Na and K–Na all correlate positively. Any possible negative correlation brought about by cation exchange dependencies is not evident in the large and variable data set. It can therefore be postulated that the concurrent increase/decrease in the cations is the result mainly of dissolution/precipitation reactions and concentration effects, while the effects of cation exchange processes are masked in the overall data set.

The pH is negatively correlated with the pCO<sub>2</sub> indicating that an increase in pCO<sub>2</sub> is generally linked to a decrease in pH. On the other hand, fluoride is positively correlated with pH, indicating that higher pH water often has a higher fluoride concentration. The high negative correlation between pH and Eh may control the solubilities of mineral phases. Eh–pH diagrams are commonly used to indicate chemical species and mobility of metals in groundwaters (Appelo and Postma, 1993; Hem, 1989).

Table 5

Results of principal component factor analysis with Varimax rotation. All values in mg/l unless otherwise indicated

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pCO <sub>2</sub> (atm)		0.729			
pH		-0.922			
EC (mS/m)	0.922				
Eh (mV)		0.916			
HCO <sub>3</sub>			0.783		
Ba					-0.799
P				0.871	
Sr	0.818				
B		-0.650			
Mn			-0.484		0.442
NO <sub>3</sub>			0.611	-0.463	
Cl	0.955				
SO <sub>4</sub>	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

### 4.3. Factor analysis

Factor analysis has proved useful as an aid in the interpretation of geochemical data (Schot and Van der Wal, 1992; Usunoff and Guzman-Guzman, 1989; Ashley and Lloyd, 1978; Dawdy and Feth, 1967). 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 inter-relations of the chemical parameters.

The hydrochemical data were analysed using R-mode factor analysis to find the main factors or processes responsible for the groundwater chemistry in the study area. Five factors account for 76.22% of the variance in the data set (Table 5). Factor 1 is interpreted as relating mainly to the salinisation of the groundwater due to both infiltration of saline surface water concentrated through evaporation and to dissolution processes. The main contributors to the groundwater salinity are Cl, Ca, Mg, Na, Sr and SO<sub>4</sub>. The main cation exchange elements Ca, Mg, Na and Sr correlate positively indicating the influence of the geological matrix. Significant positive correlations

between Ca, Sr and SO<sub>4</sub> suggest that processes of dissolution and/or precipitation of evaporitic and sulphide minerals are active. Sources of SO<sub>4</sub> could also result from redox reactions and land use practices. Though limited in extent, irrigation contributes to salt concentration and accumulation via the evapotranspiration process.

Factor 2 indicates the effect of pCO<sub>2</sub> on the pH and the known relationship (i.e. negative correlation) between pH and Eh. These parameters are known to determine the mobility and solubility of the trace elements boron and fluoride. Possible pollution of the groundwater could be related to Factor 3, given the correlation between NO<sub>3</sub> and K. Factor 4 may also be indicative of pollution through land use practices due to the presence of the biochemically related elements P, NO<sub>3</sub> and K, which are principal plant nutrients.

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<sub>4</sub>) and the rock forming mineral alkali feldspar. These minerals are common in carbonatite rocks associated with the Salpeterkop Carbonatite Complex. Manganese is probably derived from rocks containing the minerals olivine, pyroxenes and amphiboles

Table 6

Hydrochemical facies of the groundwater. Recharge: recently recharged groundwater rich in calcium and/or magnesium and carbonate. Stagnant: relatively old groundwater at the end of chemical development, with high sodium, chloride and/or sulphate values. Static discordate: groundwater that can be classified as stagnant and is actively being mixed. This water is generally rich in Ca, Mg, Na, Cl and SO<sub>4</sub>. Dynamic coordinated: water rich in bicarbonate with increasing sodium and potassium concentrations. Groundwater that is in the process of moving

Facies	Water type	Regime	Mean TDS (mg/l)
1	Ca(HCO <sub>3</sub> ) <sub>2</sub>	Recharge + static discordate	607
3	NaHCO <sub>3</sub>	Dynamic coordinate and static discordate	828
5	CaSO <sub>4</sub>	Static discordate	825
2	Na <sub>2</sub> SO <sub>4</sub>	Stagnant water	912
4	CaCl <sub>2</sub>	Static discordate + CaSO <sub>4</sub>	1176
2	NaCl	Static discordate + CaSO <sub>4</sub>	1367

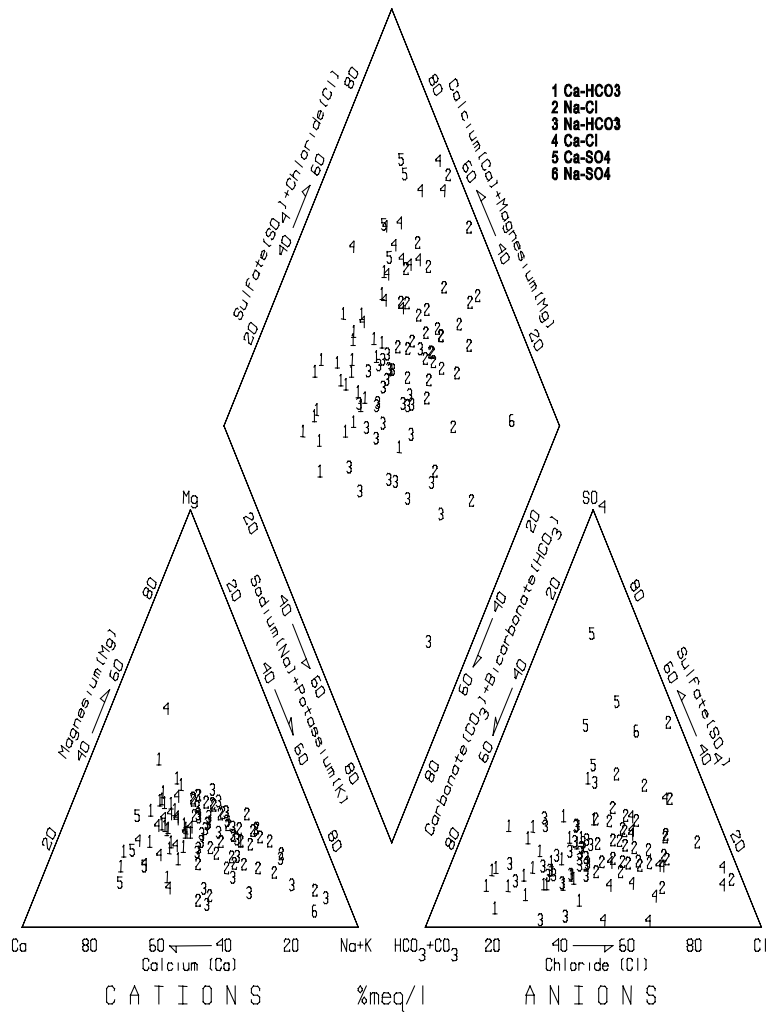


Fig. 2. Piper diagram of the groundwaters of the study area.



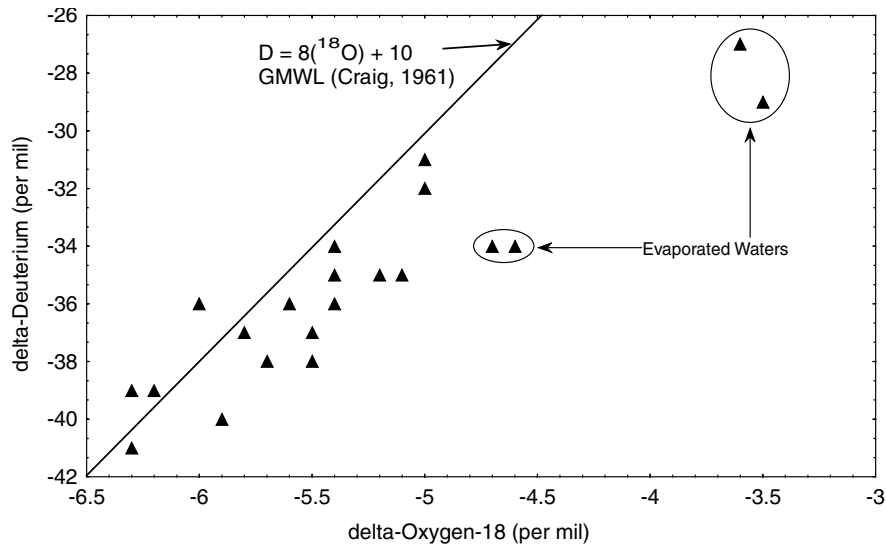


Fig. 3. Deuterium vs oxygen-18 for selected boreholes.

(Hem, 1989). Small amounts of manganese are commonly found in carbonate minerals and may substitute for calcium (Hem, 1989). Thus, manganese can also be involved in cation exchange reactions involving carbonate minerals.

#### 4.4. Groundwater types

Based on the major cation and anion, six water types are found in the study area. These are: NaCl, NaHCO<sub>3</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, CaSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> (Table 6). The chemical groundwater types of the study area were distinguished and grouped by their position on a Piper diagram (Fig. 2) (Piper, 1944; Ophori and Toth, 1988; Kirchner, 1994). The regimes in which the different waters occur in the Piper diagram are shown in Table 6. In Fig. 3, the stable isotope data are shown together with the global meteoric water line (GMWL) of Craig (1961). This clearly shows that some samples plot close to the GMWL but that others plot away from this line. Thus, the recharge of partially evaporated water takes place in some areas. In contrast, recharge in other areas seems to take place rapidly, possibly via preferred pathways, preventing any significant evaporation.

The dominant anion of the groundwater changes from bicarbonate, to sulphate to chloride with a corresponding increase in TDS (Table 6). This is

generally related to the relative age and the length of the groundwater flowpaths. Talma (1981) has shown that the trend from Ca(HCO<sub>3</sub>)<sub>2</sub> to NaCl water is associated with greater <sup>14</sup>C age in other parts of the Karoo basin. This is likely to be the case in this study area as well. The groundwaters of the area do not generally show these developments. Table 6 also indicates that the water types that are dominated by sulphates and chlorides occur in areas where there is no or very little groundwater flow. This may be due to short flowpaths caused by the various dykes that transect the study area. Ca(HCO<sub>3</sub>)<sub>2</sub> type waters occur in areas of recharge (generally topographically higher areas) and NaCl type waters in discharging and static regimes (i.e. the lower lying areas). The intermediate water types are a result of hydrogeochemical processes that occur between the two end members (Ca(HCO<sub>3</sub>)<sub>2</sub> and NaCl). Processes that may be responsible for the formation of the various water types are depicted in Fig. 4.

The formation of Ca(HCO<sub>3</sub>)<sub>2</sub> waters is primarily a result of the dissolution of carbonate minerals, whereby surface water charged with atmospheric and biogenic CO<sub>2</sub> infiltrates into the subsurface. The replacement of calcium by sodium through cation exchange results in the formation of Na(HCO<sub>3</sub>)<sub>2</sub> waters. Removal of calcium, through the precipitation of carbonate minerals, may cause a disturbance in the

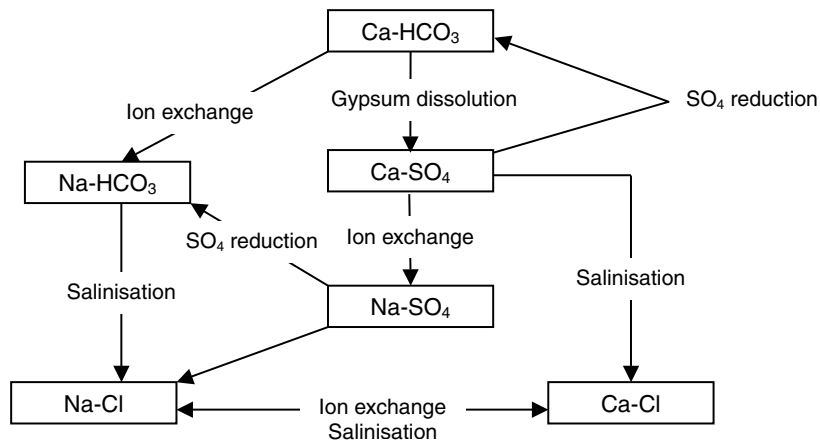


Fig. 4. Outline of the chemical processes responsible for the various groundwater types.

chemical equilibrium resulting in the dissolution of minerals containing calcium such as gypsum (Freeze and Cherry, 1979). Thus,  $\text{CaSO}_4$  type waters develop. Cation exchange processes cause the removal of Ca in solution for bound Na to form  $\text{Na}_2\text{SO}_4$  waters. Sulphate reduction of  $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$  waters leads to the formation of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{NaHCO}_3$ , respectively. Ongoing sulphate reduction is manifested in most boreholes by the presence of  $\text{H}_2\text{S}$ . Groundwater in the area is characterised by a foul smell caused by sulphate reducing bacteria, which convert sulphate into  $\text{H}_2\text{S}$ . The formation of  $\text{NaCl}$  and  $\text{CaCl}_2$  waters is a result of

progressive salinisation of the waters. At higher salinities, the process of reverse cation exchange may create  $\text{CaCl}_2$  waters due to the removal of Na out of solution for bound Ca. Alternatively,  $\text{CaCl}_2$  type waters could also be a result of the process of mixing between a “younger”, fresher water with more saline older water.

### 5. Effect of topography on the chemical and isotopic composition of the groundwaters

Because of a lack of geological profiles of the area,

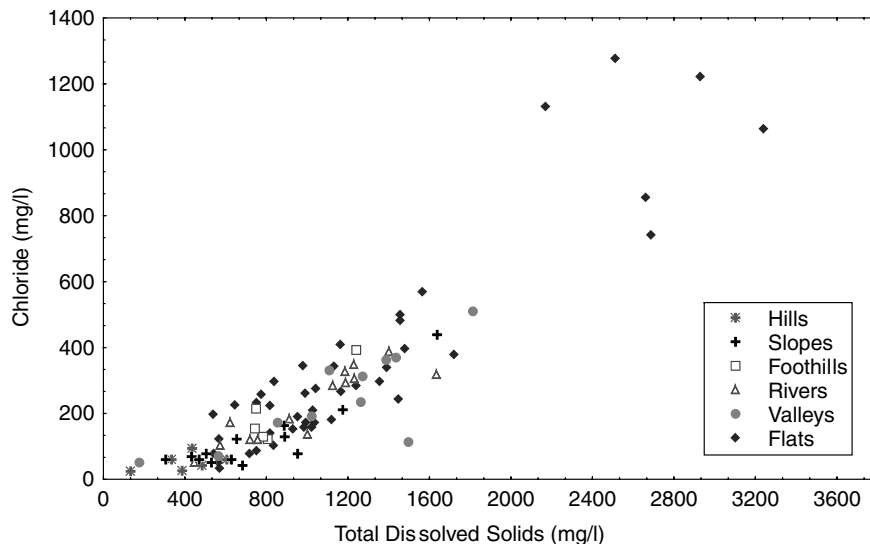


Fig. 5. Plot of chloride vs TDS and its relation to the topography.

Table 7

Average groundwater chemistry for various topographical settings. All values in mg/l unless otherwise indicated

	EC (mS/m)	pH	Cl	Na	Ca	HCO <sub>3</sub>
Hills	78	7.2	49.5	35.3	54.9	230.7
Slopes	91	7.4	125.3	114.5	72.6	310.8
Foothills	131	7.4	203.3	118.7	94.6	324.1
Rivers	138	7.4	206.3	147.5	97.1	332.2
Valleys	167	7.2	221.0	150.1	96.9	342.4
Flats	208	7.3	412.4	210.4	139	324.0

the effect of changing aquifer lithology has not yet been addressed. Enough information on the topographical settings in which the boreholes occur permits the evaluation of the influence of topography on the chemical and isotopic composition of the groundwaters.

Topography and the differences in geology (i.e. differences in hydraulic conductivities) mainly determine the rate and direction of groundwater and surface water flow. The local topography, rate of evaporation and vertical permeability typically determine the location and rate at which salts accumulate. Flat areas, riverbeds and valleys are ideal localities for the ponding of water in the study area. In topographically steeper localities (i.e. hills, slopes and foothills) more precipitation goes to runoff. From Fig. 5 it is evident that water with low Cl and TDS

values is located on hills or higher lying areas. Groundwater from valleys and flat areas has higher Cl contents and a concomitant increase of TDS. Some sampling points located on lower lying areas also show properties representing higher lying areas, indicating that topography alone does not determine the salinity of the groundwater. Factors other than residence times and evaporation, thus, also affect groundwater salinity and chemical composition. Rapid recharge through preferential pathways in lower lying areas where fractures are exposed to the surface could be a possibility.

The average concentrations of dominant ions for various topographical settings are tabulated in Table 7. Higher levels of EC, Cl, Na and Ca are found in lower lying areas. This is generally ascribed to salinisation. The Ca and HCO<sub>3</sub> values in the topographically steeper or higher lying areas are much lower than in the lower lying or flat areas and are likely to represent recent recharge without salinity build-up.

In a plot of altitude against <sup>18</sup>O content for specific boreholes (Fig. 6), a general trend emerges. Groundwater from high-altitude boreholes generally has lower <sup>18</sup>O values compared with water originating from low-altitude boreholes. This reflects the general tendency for precipitation intercepted at a high altitude to be more depleted in heavier stable isotopes than precipitation at a low altitude (Mook, 1994).

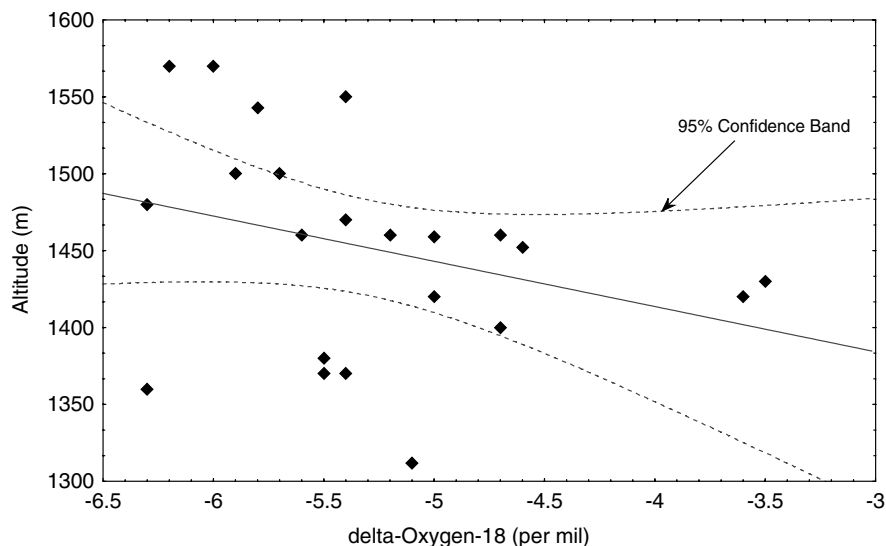


Fig. 6. Plot of altitude vs oxygen-18 for selected boreholes.

In Fig. 6 several groundwater points plot away from the regression line, indicating the overall variability of the stable isotope characteristics of groundwater (not only a function of altitude but also type, seasonality and intensity of precipitation) and also the variability of the recharge process (sources and pathways).

## 6. Conceptual model for recharge processes

Natural groundwater recharge occurs over most of the area. Recharge occurs relatively fast in some areas and in others, it is delayed. This is evident in both the major element chemistry as well as the stable isotope data.

A noticeable feature is the overlapping nature of recharge, throughflow and discharge. The configuration of the land surface is responsible for the variation in groundwater chemistry and the isotopic signature of these waters. The effect of topography on recharge is manifested by a  $\text{Ca}(\text{HCO}_3)_2$  type water in topographically higher/steeper areas where surface water ponding does not occur. These waters generally have lower pH and EC values and are dominated by the ions Ca and  $\text{HCO}_3$ . They are a direct result of incoming rainfall (with a low pH) and the subsequent dissolution of carbonate minerals (Table 7). Isotopically they lie close to the GMWL. It is also postulated that the recharge would thus occur through preferential pathways such as alongside dykes and sills and the various fracture and joint patterns that transect the study area.

In topographically flatter areas, surface water ponding occurs where enough overburden is usually present for salt accumulation because of cyclic wetting and drying. Precipitation is available for recharge ponds in these flat areas. The water is subsequently concentrated by evaporation. As the water is recharged, it leaches soluble salts in the unsaturated zone. These waters are typically characterised by an NaCl signature and an enrichment of stable isotopes (deuterium and oxygen-18) whereby they plot along a slope away from the GMWL. In topographically flatter areas groundwater with a  $\text{Ca}(\text{HCO}_3)_2$  facies also occurs. This type of water is probably a result of direct recharge through preferential pathways where ponding is absent.

## 7. Conclusions

The results of the statistical analyses, as applied to the hydrochemical data set, provide insight into the regional factors and processes controlling groundwater recharge and composition of the study area. The addition of stable isotope data for one-fifth of the sampling points provided further valuable insights. The processes that govern changes in the groundwater composition, as interpreted from the statistical and isotope interpretations, are mainly determined by the following factors:

Rainwater that is charged with biogenic  $\text{CO}_2$  as it enters the aquifer dissolves minerals and soluble salts. In topographically higher lying recharge areas, this infiltrating water dissolves mainly carbonate minerals. Water with a predominantly  $\text{Ca}(\text{HCO}_3)_2$  signature is thus found in areas of localised recharge. In topographically lower lying or flat areas, the leaching of soluble evaporitic salts, often NaCl and  $\text{CaSO}_4$ , from the unsaturated zone, and the infiltration of evaporated water are the dominant processes. Thus, NaCl type waters are predominant in lower lying areas.

The processes of dissolution, precipitation, cation exchange and sulphate reduction primarily control the formation of water types that evolve between the  $\text{Ca}(\text{HCO}_3)_2$  and the NaCl type waters. Mineral saturation state calculations indicate that the groundwaters are undersaturated with respect to fluorite, strontianite and gypsum, whereas barite and calcite reach saturation and the points are distributed equally around saturation. Cation exchange processes and sulphate reduction of  $\text{Na}_2\text{SO}_4$  waters are mainly responsible for the formation of  $\text{NaHCO}_3$  waters. Dissolution and precipitation of mineral phases determine the contribution to and removal of ionic species in solution. Precipitation of calcite causes an equilibrium disturbance in Ca concentrations and leads to the dissolution of gypsum where available. The formation of  $\text{CaSO}_4$  type water may result from this process.  $\text{CaSO}_4$  type groundwaters are also reduced to  $\text{CaHCO}_3$  waters. Cation exchange processes are responsible for the formation of  $\text{Na}_2\text{SO}_4$  type waters from  $\text{CaSO}_4$  waters. At higher salinities, reverse cation exchange may occur with

the formation of  $\text{CaCl}_2$  type water from an  $\text{NaCl}$  type. Salinisation because of long residence times causes the formation of  $\text{NaCl}$  and  $\text{CaCl}_2$  waters.

An interpretation of the chemical and stable isotopic composition of the groundwaters is complicated by the climatic variability of the area. The effect of the high evaporation rates and the local topographical conditions is responsible for the accumulation of evaporated saline waters, which subsequently infiltrate. These waters tend to mask the hydrochemical processes occurring in the subsurface.

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### References

- Appelo, C.A.J., Postma, D., 1993. *Geochemistry, Groundwater and Pollution*. Balkema, Rotterdam.
- Ashley, R.P., Lloyd, J.W., 1978. An example of the use of factor analysis and cluster analysis in groundwater chemistry interpretation. *J. Hydrol.* 39, 355–364.
- Cole, D.I., Smith, R.M.H., Wickens, H. de V., 1990. Basin plain to fluvio-lacustrine deposits in the Permian Ecca and Lower Beaufort Groups of the Karoo sequence. In: *Guidebook Gecongress'90*, Geological Society of South Africa.
- Cole, D.I., Vorster, C.J., 1999. The Metallogeny of the Sutherland Area. Explanation of Metallogenic Sheet 3220. Council for Geoscience, Pretoria.
- Coplen, T.B., 1993. Normalization of oxygen and hydrogen isotope data. *Chem. Geol. (Isotope Geoscience Section)* 72, 293–297.
- Craig, H., 1961. Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133, 1833–1834.
- Dawdy, D.R., Feth, J.H., 1967. Application of factor analysis in study of chemistry of groundwater quality, Mojaveriver Valley, California. *Water Resour. Res.* 3 (2), 505–510.
- De Wet, J.J., 1975. Carbonatites and related rocks at Salpeter Kop, Sutherland, Cape Province. *Ann. Univ. Stellenbosch, Ser. A* 1 (1), 193–232.
- Freeze, R.A., Cherry, J.A., 1979. *Groundwater*. Prentice-Hall, Englewoods Cliff, NJ.
- Harris, C., Oom, B.M., Diamond, R.E., 1999. A preliminary investigation of the oxygen and hydrogen isotope hydrology of the greater Cape Town area and an assessment of the potential for using stable isotopes as tracers. *Water S. A.* 25 (1), 15–24.
- Haughton, S.H., 1969. *Geological History of Southern Africa*. Geological Society of South Africa.
- Hem, J.D., 1989. *The study and interpretation of the chemical characteristics of natural water*. 3rd edn. USGS Water-Supply Paper 2254, US Geological Survey.
- Kirchner, J.O.G., 1994. Investigation into the contribution of ground water to the salt load of the Breede River, using natural isotopes and chemical tracers. Report No. 344/1/95. Water Research Commission, Pretoria.
- Langmuir, D., 1971. The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochim. Cosmochim. Acta* 29 (1), 1023–1045.
- Midgley, D.C., Pitman, W.V., Middleton, B.J., 1994. *Surface water resources of South Africa 1990. Book of maps — Volume 3. Report No. 298/3.2/94*. Water Research Commission, Pretoria.
- Mook, W.G., 1994. *Principles of isotope hydrology: introductory course on isotope hydrology*. Centre of Isotope Research, University of Groningen.
- Ophori, D.U., Toth, J., 1988. Patterns of ground-water chemistry, Ross Creek Basin, Alberta, Canada. *Ground Water* 27 (1), 20–55.
- Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water analyses. *Trans. Am. Geophys. Union* 25, 914–923.
- Plummer, L.N., Prestemon, E., Parkhurst, D.L., 1992. An interactive code (NETPATH) for modelling net geochemical reactions along a flow path. USGS Water Resour. Inv. Rep. 91-4078, US Geological Survey.
- Schot, P.P., Van der Wal, J., 1992. Human impact on regional groundwater composition through intervention in natural flow patterns and changes in land use. *J. Hydrol.* 134, 297–313.
- Smith, R.M.H., 1990. A review of stratigraphy and sedimentary environments of the Karoo Basin of South Africa. *J. Afr. Earth Sci.* 10 (1/2), 117–137.
- Swan, A.R.H., Sandilands, M., 1995. *Introduction to Geological Data Analysis*. Blackwell, Oxford.
- Talma, A.S., 1981. Chemical changes in groundwater and their reaction rates. *Trans. Geol. Soc. S. A.* 84, 99–105.
- Theron, J.N., 1983. *Die geologie van die Gebied Sutherland. Toeligtig van Blad 3220*. Geologiese Opname, Pretoria.
- Usunoff, E.J., Guzman-Guzman, A., 1989. Multivariate analysis in hydrochemistry: an example of the use of factor and correspondence analysis. *Ground Water* 27 (1), 27–34.
- Venter, J.M., Mocke, C., De Jager, J.M., 1986. Climate. In: Cwilling, Roux, Pieterse (Eds.), *The Karoo biome: a preliminary synthesis. Part 1 — Physical environment*. South African National Scientific Programmes Report No. 124. Foundation for Research and Development.
- Visser, J.N.J., Loock, J.C., Jordaan, M.J., 1980. Permian Deltaic sedimentation in the western half of the Karoo Basin, South Africa. *Trans. Geol. Soc. S. A.* 82, 415–424.