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Groundwater as an alternative source to irregular surface water in the O'Kiep area, Namaqualand, South Africa

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ABSTRACT

Water insecurity is a growing concern globally and the role of groundwater and aquifers in buffering the effects of climate variability and change is increasingly acknowledged due to extended periods of drought in arid regions. Water security can only be fully realised with a more robust understanding of groundwater as a water resource, especially in the O'Kiep area which is in Namaqualand, South Africa. Results of analyses of groundwater samples ($n = 8$) indicated that pH values met acceptable standards for drinking, while the total dissolved solids (TDS) and electrical conductivity (EC) were however not within the recommended limits. The chemical composition of the groundwater indicated Eh values −34.1 to −87.2 mV, indicative of reducing geochemical conditions with the most abundant ions being Cl^-, SO_4^{2-}, NO_3, F^-, Na^+, Ca^{2+}, Mg^{2+} and K^+. Furthermore, some of the ions were not within the guidelines, i.e. Cl^-, SO_4^{2+}, Na^+, Ca^{2+} and Mg^{2+}, but all the potential toxic elements, namely: Al, S, As, Cd, Cr, Co, Cu, Fe, Mn, Hg, Ni, Se, V, Zn and CN, were within acceptable values for drinking groundwater as recommended by the SANS241-1 (2015) and WHO (2011). Hydrogeochemical characteristics of the water indicated that the continuous consumption of the groundwater without pretreatment might result in possible human health risk as the Groundwater Quality Index (GWQI) confirmed that the groundwater quality could be classified as being of moderate concern. Furthermore, the hydrogeochemical indices ($CaCO_3$/Cl and Mg/Ca) and cationic exchange values indicated that the aquifer is of inland origin while the piper trilinear diagram revealed that the groundwater type in the area is categorised as sodium – potassium – chloride – sulphate- (Na–K–Cl–SO_4), carbonate – chloride – sulphate- ($CaCO_3$–Cl–SO_4) and sodium – chloride (Na–Cl) type water. Additionally, the Sodium Adsorption Ratio (SAR) values up to 11.7 indicated that the groundwater is brackish and its excessive usage may have undesirable effect on plant growth. Therefore, this study recommends the consideration of suitable measures to improve the GWQI for the benefit of the community which have access to limited water resources.

1. Introduction

Groundwater is often the preferred source for drinking water since it is acceptable to various communities as it is often free from odour. It is often considered to be the best alternative to tap water due to its natural protection from contamination when compared to surface water. It is perceived to be low in contamination due to its low turbidity (Edokpayi et al., 2018). Despite the perceived safety associated with groundwater consumption, several researchers have shown that groundwater can also be susceptible to contamination (Chakraborti et al., 2016; Indelicato et al., 2017). Several factors that influence the groundwater quality index (GWQI) include the climate, geology of the aquifer and anthropogenic activities such as mining in the locality of the aquifer (Aslam et al., 2018; Lee et al., 2017). In the peri-urban and rural areas, most of the groundwater is usually untreated. It has been reported that it is difficult for groundwater to purify itself to acceptable standards and is very expensive to treat (Edokpayi et al., 2018).

Several studies have been published in Namaqualand regarding the

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area's groundwater quality, with a high fluoride concentration being reported by Abiye et al. (2018) and Abiye and Leshomo (2013). These studies investigated the groundwater flow, its radioactivity and metal enrichment. Erdogan et al. (2017) also reported on the hydrochemical characteristics of the open-pit groundwater in O'Kiep, which is contaminated with acid rock drainage (ARD). Additionally, ARD can persist more than 10 km from its source and might have an impact on groundwater bodies of neighbouring areas (Naicker et al., 2003), further contributing to the challenges as it contains various types of potentially toxic elements (PTEs) such as Cd, Cu, Cr, Pb, Ni, F, As and Zn. These PTEs may accumulate in water bodies and could form critical long-term hazards for groundwater.

Négrel et al. (2007) indicated that the mixture of contaminant transference into groundwater up to the depth of 50 m underneath the surface, is feasible. A study conducted by Giri et al. (2017) also justified that 50% of the groundwater is highly contaminated with respect to PTEs such as Cu, Ni, Co, Cr, Mn and Pb in the vicinity of a copper mining area, which suggests a possible way for human exposure (Singh et al., 2018), particularly whereby groundwater is an altertive source of drinking water. As a result, the use of groundwater sources of unknown quality puts the consumers at risk to possible waterborne diseases (Edokpayi et al., 2018). These contaminants can enter the human body through various pathways such as inhalation and through skin absorption. Once they enter the human body, a majority of PTEs are adsorbed and bio-accumulate in the human body, culminating in the development of a range of illnesses due to long-term exposure (Avigliano and Schenone, 2015).

O'Kiep is located in the Namaqualand area, which is characterised as being an arid environment whereby groundwater is the only alternative source of water supply for the community living there (Erdogan et al., 2017). Also, this former copper (Cu) mining town has challenges with chronic water shortages. Therefore, groundwater resources offer an opportunity to improve resilience against recurring droughts due to inadequate potable water supply and to mitigate general drinking water insecurity. Extensive mining of Cu-ore has left a legacy of contaminated mine waste heaps and mine tailings distributed throughout the copper mineral belt in the O'Kiep area. The hazards caused by mine waste, especially the deterioration of groundwater quality in this area (Erdogan et al., 2017), can culminate in negative human health clinical outcomes. The aim of the study was to assess the quality of groundwater and to determine its suitability for domestic and irrigation purposes.

2. Materials and methods

2.1. Geology and hydrogeology

The primary copper bearing minerals are chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4) and other minerals including biotite, plagioclase, quartz, and magnetite. The copper content of the Koperberg Suite in O'Kiep, is erratic, with embedded PTEs (Wulfse and Holdsworth, 1994; Stumpfl et al., 1976). The geology of O'Kiep has also been described as comprising of intrusive rocks, consisting of a thick sheet of granite (Abiye and Leshomo, 2013; Clifford and Barton, 2012). In the study of granulite facies transition in the O'Kiep area by Raith and Meisel (2001), two types of metabasites were determined to be arising along the granulite amphibolite facies. The southern granulite facies of the O'Kiep includes Mg-rich ol-normative forms and low-MgO ores. The O'Kiep area is characterised by an arid to semi-arid climate which has direct impact on the effective recharge (Abiye and Leshomo, 2013), with groundwater occurring from a fractured, crystalline basement and an alluvial aquifer, which is efficiently recharged during the rainy season. The climate is further influenced by an altitude, topography and distance from the sea (Xu and Beekman, 2019; Adams et al., 2004). The aquifer extent and distribution in the area is largely controlled by the tectonics, fracture frequency, distribution of alluvial sediments and weathering zones (Abiye and Leshomo, 2013). The thickness and characteristics of the composite aquifer varies from one site to another, particularly in relation to its petrographic composition of respective rocks, their type, including their ectonic deformations due to weathering effects and changing climatic conditions (Adams et al., 2004).

2.2. Study area and data collection

Groundwater samples (n = 8) were collected in June 2018 during the winter season with minimal rainfall of approximately 2 mm and with ambient temperatures averaging 6 °C (Accuweather, 2018). GPS coordinates were used to demarcate sampling sites as presented in Fig. 1.

Groundwater samples were collected according to the groundwater sampling guidelines as described by Nielsen and Nielsen (2006). The groundwater samples were collected near the well head of each of the boreholes. The boreholes in this study ranged from 30 to 150 mbgl in depth and pumping rate of approximately 0.5 L/s, which was also confirmed by Titus et al. (2002), with boreholes B1, B2, B3, B6 and B8 ranging between 13 and 25 km apart, while B5, B4 and B7 between 6 and 8 km apart. The samples were collected after 15 min of pumping and a maximum of three samples were collected into sterile 1L schott Duran bottles per visit to minimise possible sample deterioration, which might affect the sampled groundwater chemistry. Multi-parameter instruments and sensors were calibrated prior to field measurements used according to national field water measurement standards Li and Migliaccio (2010). Bottles were also rinsed with sample water prior to sampling.

During sampling, the following physical parameters were quantified on-site, namely temperature, pH, electrical conductivity, redox potential and totally dissolved solids, using an EXSTIK II® EC500 to minimise atmospheric variations (Weaver et al., 2007; Sundaram et al., 2009). Samples were also filtered through a 0.45-μm pore-size cellulose membrane using a hand-vacuum pump into 1L schott Duran bottles (APHA et al., 2012). The unfiltered samples were digested with technical grade nitric acid (0.2 M) at $pH < 2$. Unless otherwise stated, all reagents used were of analytical grade standard, while standardised analysis methods were used (APHA et al., 2012). All samples were stored in cooler boxes with ice to ensure their preservation during transportation to the laboratory where further analyses were performed. All samples were analysed without dilution. Analyses were performed to measure the concentrations of anions, cations, trace elements and chemical oxygen demand, using a UV–Vis spectrophotometer, an inductively coupled plasma (ICP) either attached to a mass spectrometer (MS) or an optical emission spectrometer (OES) and a high-performance liquid chromatography (HPLC), at an external South African nationally accredited laboratory.

2.3. Data treatment

Multivariate statistical analyses were used for the assessment of the groundwater quality and flow. The most commonly used methods and software used in the analyses included MSOffice Excel2016®, Cation and Anion Balance (CAB) and Cationic Exchange Values (CEV), Groundwater Quality Index (GWQI), Sodium Adsorption Ratio (SAR) and a trilinear piper plot.

Analysed groundwater samples showed that the value of computed CAB error (Eq. (1)) adopted from Domenico and Schwartz (1998), was 2.4% which was within the acceptable limit of ±5%.

$$\text{Cation and Anion Balance (CAB)} = \frac{TC - TA}{TC + TA}\, x\ 100 \tag{1}$$

where, TC = total cations and TA = total anions.

Cationic Exchange Values (CEV) of the groundwater as described by Nwankwoala and Ememu (2018) and Abadom and Nwankwoala (2018) were calculated using Eq. (2):

$$\text{Cationic Exchange Values (CEV)} = \frac{Cl - (Na + K)}{Cl} \times \frac{Mg}{Ca} \tag{2}$$

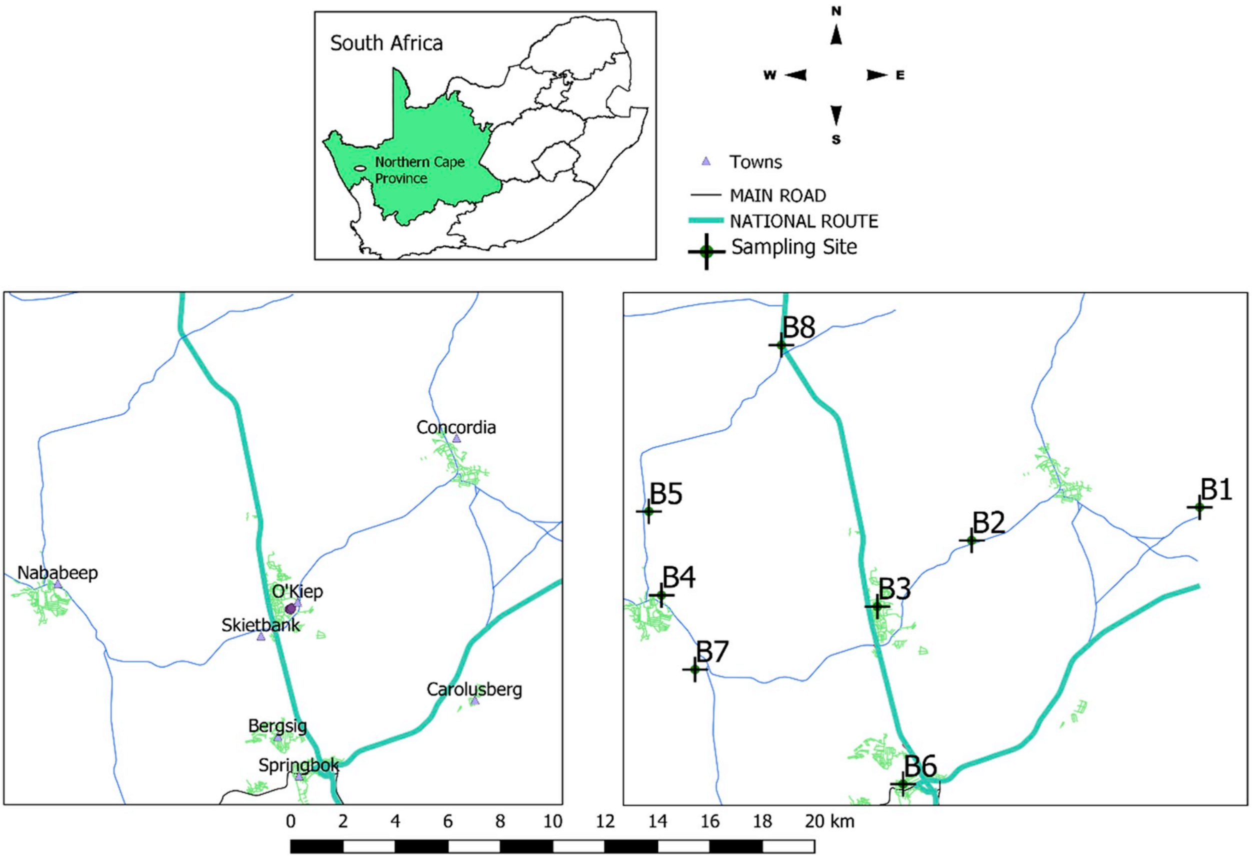

Fig. 1. Study area and sampling points: drawn using Geological maps were generated using Quantum GIS software (v. 2.18.11) and data from National Geo-Spatial Information (NGI), a component of the Department of Rural Development and Land Reform, South Africa.

2.4. Groundwater quality index (GWQI)

Assessment of groundwater quality status was done by using the GWQI method, which is an effective tool to assess spatial and temporal changes in groundwater quality. GWQI was calculated according to the mathematical expression for National Sanitation Foundation as reported in Rickwood and Carr (2007) and Tyagi et al. (2013) - see Eq. (3).

$$\mathrm{GWQI} = \sum_{t=1}^{n} \mathrm{Q_i W_i} \tag{3}$$

where:

Q_i = sub index of the water quality parameter
W_i = weight associated with the water quality parameter
n = number of quality parameters

The parameters used were pH, temperature, turbidity, total phosphorus and nitrates (number of quality parameters used was five, $n = 5$). The index generates a number between 1 and 100, with one (1) being the poorest and hundred (100) indicating excellent water quality. The ratings were defined using the following categories as presented in Table 1:

Table 1
Groundwater quality index guidelines (Rickwood and Carr, 2007; Tyagi et al., 2013).

Category of Groundwater Quality	Groundwater Quality index
Excellent groundwater quality	91–100
Good groundwater quality	71–90
Medium groundwater quality	51–70
Bad groundwater quality	26–50
Very bad groundwater quality	0–25

2.5. Classification of irrigation groundwater quality

In this study, the groundwater quality with respect to irrigation was assessed by the following methods: Sodium Adsorption Ratio (SAR) and Magnesium (Mg) hazard. Hence, to consider the groundwater suitability for irrigation the assessment of sodium concentration was essential. The sodium or alkali hazard in the use of water for irrigation was determined by the absolute and relative concentration of the cations in the groundwater. The relative activity of sodium ion in the exchange reaction with soil was expressed in terms of SAR. The SAR, which indicated the effect of relative cation concentration on Na^+ accumulation in the soil, was used for evaluating the sodicity of irrigation water. The sodicity hazard of water is generally described by the SAR (Adimalla and Venkatayogi, 2018) as shown in Eq. (4).

$$\text{Sodium Adsorption Ratio (SAR)} = \frac{\mathrm{Na}}{\sqrt{\mathrm{Ca} + \mathrm{Mg}/2}} \tag{4}$$

Classification of irrigation groundwater quality, with respect to salinity hazard and sodium hazard was according to method reported in Richards (1969).

3. Results

The hydrogeochemical results of the groundwater are presented in Table 2, including a comparison with the standard guideline values as recommended by the World Health Organization (WHO, 2011) and South African National Standards (SANS241-1, 2015) for drinking and public health which was undertaken in order to have an overview of the

Table 2
Statistical summary of the hydrogeochemical parameters compared to drinking groundwater standard SANS241-1 (2015) and WHO (2011).

Parameters	Units	Min.	Max.	Av.	(SANS241-1, 2015)	WHO (2011)
Chemical Oxygen Demand (COD)	mg/L	14.6	18.0	15.0	–	20
Alkalinity ($CaCO_3$)	mg/L	51.4	333	134	–	–
pH	–	7.41	9.55	8.1	$5 \leq 9.7$	6.5–9.5
Temperature	°C	14.20	16.1	15.0	–	–
Electrical conductivity (EC)	mS/cm	43.3	476	241	≤170	100
Turbidity	NTU	0.2	196	27	≤5	–
Redox Potential (Eh)	mV	- 87.2	- 34.1	- 57	–	–
Total Dissolved Solids (TDS)	mg/L	303	3874	1793	≤1200	500
Calcium (Ca)	mg/L	31.3	384	184	–	–
Sodium (Na)	mg/L	27.6	501	243	≤200	100
Magnesium (Mg)	mg/L	12.4	142	67.3	–	–
Potassium (K)	mg/L	2.1	44.4	15.3	–	–
Chlorine (Cl)	mg/L	23.0	1255	470	≤300	5
Fluoride (F)	mg/L	0.10	2.03	1.33	≤1.5	1.5
Sulphate (SO_4)	mg/L	43.4	1210	455	≤500	200
Ammonia (NH_3)	mg/L	0.16	0.16	0.16	≤1.5	–
Nitrate (NO_3)	mg/L	0.10	7.80	2.16	≤11	–
Phosphate (P)	mg/L	0.50	0.50	0.50	–	0.4
Aluminium (Al)	mg/L	0.05	0.05	0.05	≤0.3	–
Antimony (S)	mg/L	0.02	0.02	0.02	≤0.02	–
Arsenic (As)	mg/L	0.01	0.01	0.01	≤0.01	0.001
Cadmium (Cd)	mg/L	0.003	0.003	0.003	≤0.003	–
Chromium (Cr)	mg/L	0.01	0.01	0.01	≤0.05	–
Cobalt (Co)	mg/L	0.01	0.01	0.01	≤0.5	
Copper (Cu)	mg/L	0.01	0.13	0.03	≤2	1
Iron (Fe)	mg/L	0.05	0.23	0.07	≤2	0.3
Manganese (Mn)	mg/L	0.01	0.12	0.02	≤0.4	0.05
Mercury (Hg)	mg/L	0.01	0.01	0.01	≤0.006	–
Nickel (Ni)	mg/L	0.02	0.02	0.02	≤0.07	–
Selenium (Se)	mg/L	0.04	0.13	0.06	≤0.04	–
Vanadium (V)	mg/L	0.01	0.01	0.01	≤0.2	–
Zinc (Zn)	mg/L	0.00	0.01	0.00	≤5	2
Cyanide (CN)	mg/L	0.00	0.01	0.01	≤0.2	–

groundwater quality of O'Kiep.

4. Discussion

4.1. Hydrogeochemical characteristics of groundwater

The groundwater quality challenges usually result from a high composition of anions and cations with elevated concentrations of PTEs being a concern, which renders the groundwater unsafe for numerous anthropogenic purposes, in particular drinking. The groundwater was alkaline with a median pH value of 8.1 and was within the acceptable guidelines stipulated by SANS241-1 (2015) and WHO (2011). The $CaCO_3$ in samples was classified as of low alkalinity to moderately hard (Sawyer and McCarty, 1967), with its range being 51.4–333 mg/L, a profile attributed to the groundwaters' flow through the surface and subsurface of carbonate layers in the aquifer (Abboud, 2018; Rao et al., 2012). This is an indication of brackish and hard groundwater (Zhang et al., 2018). Similarly, the EC concentration values for B1, B2, B3, B5, B7 and B8 ranged between 178 and 476 mS/cm, which were above SANS241-1 (2015) guidelines for drinking water. However, these high EC values may not be an indication of the presence of toxic dissolved metalloids in the groundwater as locally elevated ECs are common in any hydrogeological settings (Tessema et al., 2014).

The alkaline pH and high EC values are well documented in the Namaqualand region (Nell and van Huyssteen, 2014). Another important indicator of groundwater quality is TDS, with its fluctuation being attributed to the dissolution of minerals in the rock of the aquifer. TDS concentrations above the SANS241-1 (2015) were observed for samples from B1, B2, B3, B5, B7 and B8 with TDS ranging between 1248 and 3874 mg/L; while B4 and B6 had EC and TDS concentrations that were within the guidelines stipulated by both the SANS241-1 (2015) and WHO (2011). Abboud (2018) indicated that TDS greater than 1000 mg/L in groundwater is a characteristics of brackish type water. Generally, TDS and EC are dependent on the characteristics of the aquifers' geological formation (Tessema et al., 2014) with higher EC and TDS in the study area being an indication of a salt-enriched environment with the leaching of salts from soils and the rocks into groundwater being prevalent (Prasanth et al., 2012), an indication that the groundwater is not suitable for drinking.

Similarly, Eh values of −34.1 to −87.2 mV were indicative of geochemical conditions being predominantly reductive (Soldatova et al., 2017; Pirajno, 2012). The crucial consequence of the decrease of Eh could be a shift in a balance of nitrogen species in the groundwater of the study area (Sun et al., 2014). The Eh and pH are also important parameters which control the mobility of elements in geological systems (Pirajno, 2012). Furthermore, turbidity values of B2 and B6 were 196 and 18.8 NTU, respectively, which were determined not to be within the guidelines of SANS241-1 (2015) and WHO (2011). High turbidity is a common phenomenom in shallow-water environments that experience periodic alteration of ecological interactions and weathering conditions (Niu et al., 2018). The COD of groundwater ranged between 14.6 and 18.0 mg/L averaging 15.0 mg/L, which was indicative of a restoration of the dissolved oxygen in the groundwater systems (Jayalakshmi et al., 2011). According to WHO (2011), the desirable limit of COD is 20 mg/L. The concentration of COD at all sampling sites were shown to be within the limit of the WHO (2011) standards.

The most abundant cations were Ca^{2+}, Mg^{2+}, Na^+ and K^+. Ca^{2+} with Mg^{2+} concentration values of 31.3–384 mg/L and Mg^{2+} being from 12.4 to 142 mg/L. These were expected as a high Mg^{2+} concentration could also be due to the geology of the study area with southern granulite facies including Mg-rich forms and a low-MgO structure display of mineralised composites consisting of MgO up to 19.7 wt % (Maier et al., 2012; Maier, 2000), with an average of 67.3 mg/L. According to Afolabi Olubukola et al. (2018), Mg^{2+} occurs in natural water, but its concentration is always lower than that of Ca^{2+}, which seems to be the case in the study area. The principal sources of Ca^{2+} and Mg^{2+} in groundwater samples are detrital minerals such as plagioclase amphibole, feldspar, garnet and pyroxene (Srinivas et al., 2017). (Clarke et al., 2014), Lombaard et al. (1986) and Schoch and Conradie (1990) reported that the source of Mg^{2+} could be due to the mafic nature of the ore body, which consist of pyroxenitic and noritic variations of the Koperberg Suite. The Na^{2+} concentrations for B1, B2, B3, B5, B7 and B8 ranged from 134 to 501 mg/L and were not within the permissible concentration values for drinking water as indicated by SANS241-1 (2015) and WHO (2011). Additionally, the Na^+ and K^+ can be attributed to a contribution from geogenic activities such as the weathering of ferromagnesian minerals, i.e. feldspars and mica (Srinivas et al., 2017).

The most abundant anions in B1, B2, B3, B4, B5, B7 and B8 samples were Cl^- (23.0 and 1255 mg/L) and SO_4^{2-} (213–1210 mg/L) with these anions being above the permissible drinking water guidelines recommended by SANS241-1 (2015) and WHO (2011). A high concentration of both SO_4^{2-} and Cl^-, can be attributed to the oxidation of sulphidic minerals taking place due to dominant sulphidic ores being present in the area (Erdogan et al., 2017). The concentration values for B2, B3, B4, B5,B7 and B8 for NO_3^- (1.1–7.8 mg/L) were shown not to be within the limit of the WHO standards and no geological origin for NO_3 exists in the area as reported by Adams et al. (2004). The concentration values of F^- (1.33) from all samples were within the drinking water guidelines recommended by SANS241-1 (2015) and WHO (2011). However, lifetime exposure to F- can results in dental fluorosis as previously reported by Abiye et al. (2018) and Pietersen et al. (2009), as this anion tend to occur where fluorine-bearing minerals are abundant in the fractured rock aquifers, which is the case in Namaqualand as reported by Pietersen et al. (2009). Additionally, all the PTEs such as Al, S, As, Cd, Cr, Co, Cu, Fe, Mn, Hg, Ni, Se, V, Zn and CN were all below 0.2 mg/L, which were within the standardised drinking groundwater guidelines. The GWQI of 52 indicated that the groundwater quality of the study area was a moderate concern (Tyagi et al., 2013).

4.2. Groundwater interactions and hydrogeochemical relations

The Gibbs diagram suggested by Gibbs (1970) is used to differentiate the dilution, evaporation and rock weathering as hydrogeological processes affecting the groundwater of the aquifer. Gibbs' diagram (Fig. 2 A and B) for chemical data combines evaporation and chemical weathering as interlinked phenomena. This study suggests evaporation means concentration by dissolution that occurs in case of no dilution, because the concentration process is reasonably more effective in groundwater. Similar results were also obtained in a study by Awadh et al. (2016) since the aquifer in the study area is mainly controlled by weathering reactions. Gibbs' diagram displayed a minimal dilution process which reflects a lack of precipitation in the recharge area that feeds the aquifer. The Na/(Na + Ca) ratios ranged between 0.5 and 0.6, which is an indication that carbonate minerals do dominate since groundwater chemistry tends to be driven to lower Na/(Na + Ca) ratios (Marandi and Shand, 2018).

4.3. Hydrogeochemical indices and cationic exchange values for groundwater

Table 3: Hydrogeochemical indices and cationic exchange values for the groundwater.

The hydrogeochemical index values of $Cl/CaCO_3$ (0.2–11) indicated that inland groundwater values between 0.1 and 5 are attributed to inland-based water sources, while sea water ranges between 20 and 50 (Nwankwoala and Udom, 2011). Values of CEV specified for inland waters are close to zero and, for seawater, are +1.2 to +1.3 (Al-Mashakbeh, 2017). Additionally, the CEV values in the study area were below 1.0, ranging from −0.2 and 0 indicating that the groundwater in

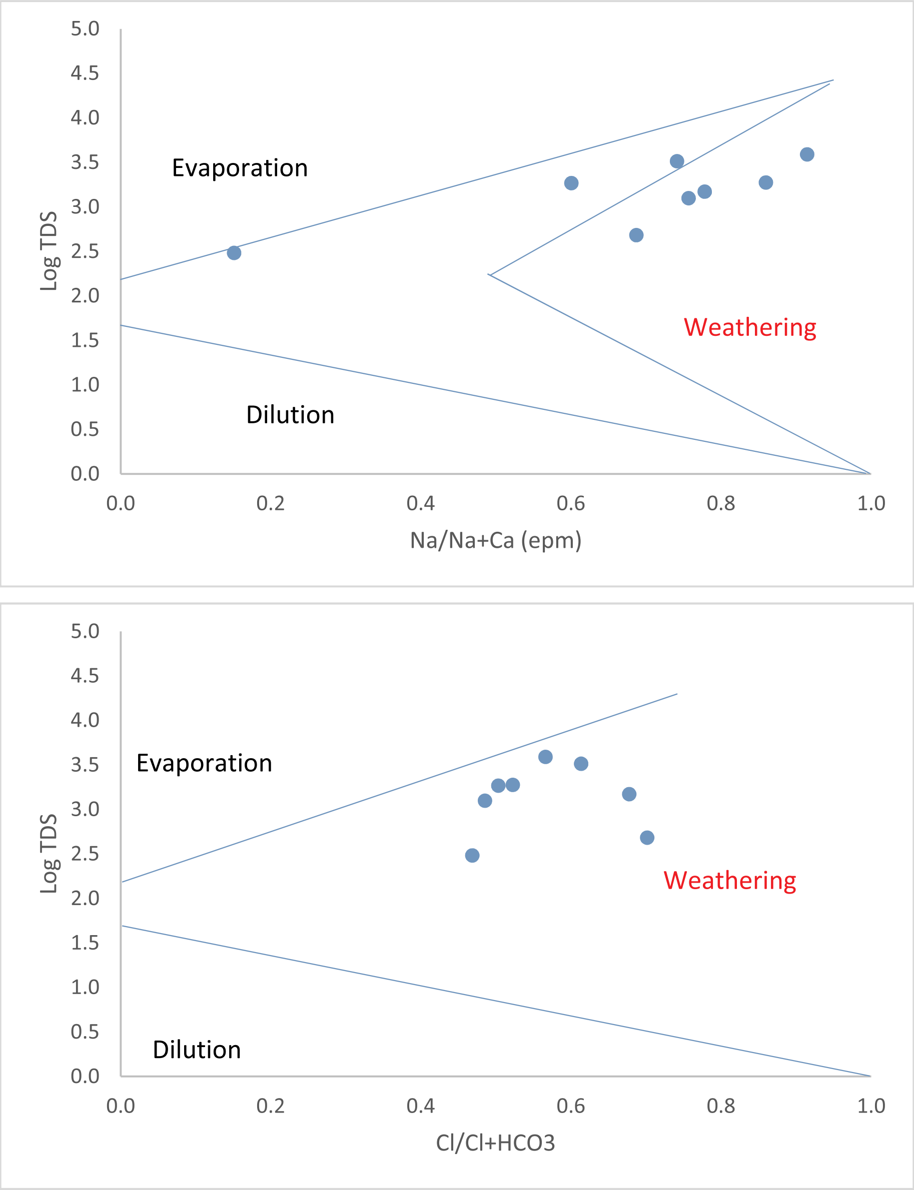

Fig. 2. A and B; the Gibbs diagrams classification of groundwater samples of the aquifer of the study area.

Table 3
Ionic Ratios and Cationic Exchange Values (CEV) for groundwater.

Sample No	B1	B2	B3	B4	B5	B6	B7	B8
$CaCO_3$/Cl	0.3	0.3	0.2	4.6	0.7	0.5	0.3	0.1
Na/Ca	0.9	2.1	1.1	0.9	1.0	2.4	1.6	1.3
Ca/Cl	0.4	0.3	0.6	1.4	1.2	0.3	0.3	0.3
Mg/Cl	0.1	0.1	0.1	0.6	0.7	0.1	0.1	0.1
K/Cl	0.004	0.003	0.005	0.004	0.010	0.002	0.002	0.001
SO_4/Cl	0.5	0.7	1.9	1.9	6.5	0.8	0.5	0.4
Mg/Ca	0.3	0.5	0.2	0.5	0.6	0.4	0.5	0.2
Ca/SO_4	0.7	0.4	0.3	0.7	0.2	0.3	0.6	0.8
CEV	0.2	0.2	0.0	−0.2	−0.2	0.1	0.3	0.1

the study area appeared to be of an inland origin, because waters under marine influence would have CEV's of around 5 (Nwankwoala and Udom, 2011). On the other hand, Mg/Ca values of 0.2–1.0 indicated a complexity between Mg^{2+} and Ca^{2+} due to their interactions with rocks (Naseem et al., 2010) and the arid climate in the study area (Erdogan et al., 2017). As such, the hydrogeochemical indices ($CaCO_3$/Cl and Mg/Ca) and CEV's indicated that the groundwater chemistry was due to the rock weathering of minerals, as the aquifer of the area is comprised of more fractured and higher permeability rock with exposure to loamy sand soils (Musekiwa and Majola, 2013).

4.4. *Geochemical classification of groundwater (piper plot)*

The hydrogeochemical facies interpretation is a tool for determining the flow pattern and the origin of chemical species of groundwater (Back, 1966), which reflects the effect of chemical processes occurring between the minerals within the subsurface rock units and the groundwater as presented in Fig. 3.

The representation of chemical results on a Piper trilinear diagram (Fig. 3) shows that the groundwater evolves towards SO_4^{2-} since O'Kiep mainly comprises Cu-rich sulphide minerals dominated by chalcopyrite and bornite (Maier, 2000; Maier et al., 2012). The study area shows that there is a mixture of three types of groundwater with variable concentrations of major ions. These are based on major ion data, the chemical composition of the groundwater sampled with three major groups in the region of B1, B2, B3, B5, B7 and B8 sodium – potassium – chloride – sulphate (Na–K–Cl–SO_4) water type, while B4 falls within carbonate – chloride – sulphate ($CaCO_3$–Cl–SO_4) water type. Furthermore, the presence of carbonate in this factor indicates localised recharge as HCO_3 is primarily derived from the dissolution of carbonate minerals by slightly acidic rainwater (Adams et al., 2004). However, Abiye et al. (2018) reported that the groundwater in the Namaqualand falls within Na–Cl water type. The diamond also confirmed a water type of Na– Cl origin, which was attributed to preferential dissolution and leaching of the more evaporitic salts during infiltration (Adams et al., 2004).

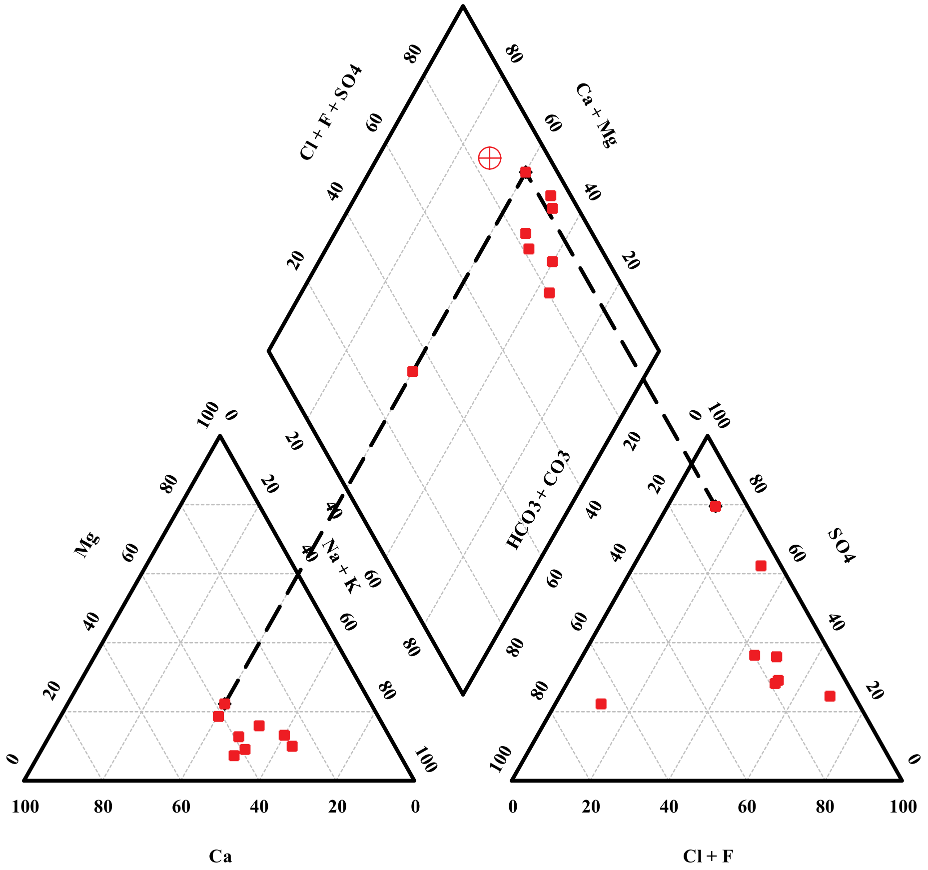

Fig. 3. Piper trilinear diagram for groundwater classification in the area.

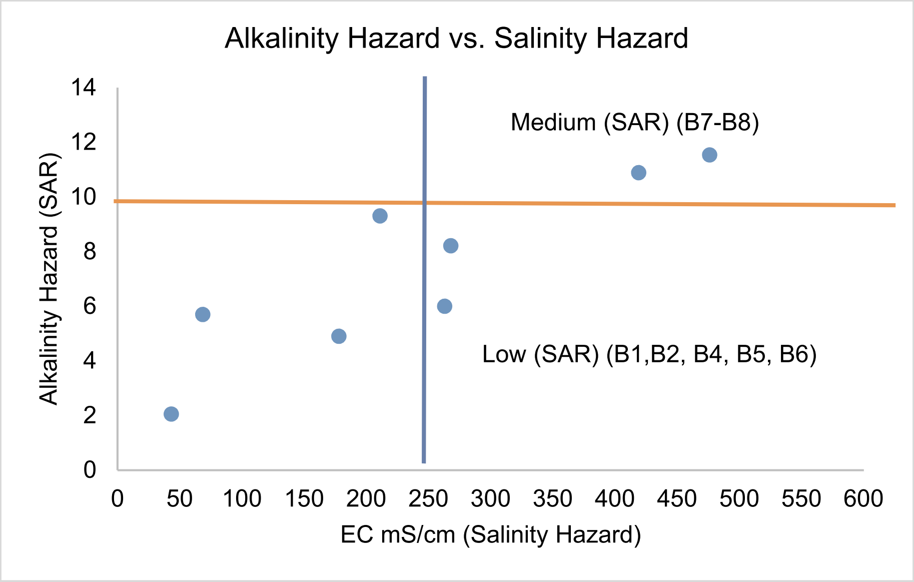

Fig. 4. Classification of irrigation waters.

4.5. Groundwater for irrigation

The groundwater quality with respect to irrigation is presented in Fig. 4. The groundwater for B1–B4 was classified as a low salinity hazard, with B7– B8 samples being of a medium salinity hazard. The alkalinity hazard for B1, B2, B4, B5 and B6 was less than 10; whereas, for B7–B8 samples, medium alkalinity hazard was allocated as the classification was above 10. Additionally, SAR values for B1, B2, B3, B4, B5 and B6, i.e. 2.0 to 9.2, classified the samples as of low salinity, whereas for B7 and B8, the classification of medium salinity was assigned; although, the groundwater in the study area can be classified as of medium to low alkalinity. Excess usage may have an undesirable effect on plant growth.

5. Conclusions and recommendations

The groundwater quality data indicated that the following PTEs, namely; Al, S, As, Cd, Cr, Co, Cu, Fe, Mn, Hg, Ni, Se, V, Zn and CN, were within the acceptable range for drinking groundwater standards set-out by the SANS241-1 (2015) and WHO (2011). The groundwater was classified as being of a low to medium alkalinity as well as having low to high hardness due to the $CaCO_3$ concentration in samples, indicating that the groundwater is brackish. The TDS, EC, Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+} were not within the drinking groundwater guidelines. TDS and EC which are depend on the characteristics of the geological formation in the study area, were higher, indicating leaching of salts from the aquifer into the groundwater, with the lowest Eh values being indicative a reducing environment. The crucial consequence of the decrease of redox potential could be a shift in a balance of nitrogen species in the groundwater of the study area. The most abundant anions and cations in the study area were Cl^-, SO_4^{2-}, NO_3^{2-} and F^- and Na^+, Ca^{2+}, Mg^{2+} and K^+ with a GWQI classification indicating that the groundwater contamination was of moderate concern. Former mining activities were assumed to have contributed to O'Kieps' groundwater contamination and its quality.

The aquifer in this study area was detyermined to be controlled by weathering reactions, with minimal dilution processes, which reflects lack of precipitation in the recharge area that feeds the aquifer. Also, the Mg/Ca ratios indicated the complexity between Mg^{2+} and Ca^{2+}, an interaction generally observed in arid regions. The groundwater type in the area was categorised as sodium – potassium – chloride – sulphate (Na – K– Cl – SO_4), carbonate – chloride – sulphate ($CaCO_3$ – Cl – SO_4) and sodium – chloride (Na – Cl) groundwater type, with the water further being classified as being of low to medium salinity and therefore, an alkalinity hazard. However, excess usage for irrigation purposes may have an undesirable effect on plant growth. Further water quality problems arise as a result of the contamination of groundwater from anthropogenic activities such as mining. Furthermore, the high TDS, EC, Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+}, suggested that strategies and appropriate remediation and rehabilitation protocols are required to improve the current challenges in the study area. This would include the implementation of in-situ groundwater monitoring, remediation and desalination technologies, if the groundwater is to be used for drinking and agricultural purposes. Lastly, improved management of groundwater resources in O'Kiep will lead to a more reliable and maintainable resource. Therefore, this study suggests regular monitoring of boreholes in the area to improve the groundwater quality prior to drinking and irrigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.pce.2019.09.003.

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