



Seasonal variation of hydrochemical characteristics of open-pit groundwater near a closed metalliferous mine in O’Kiep, Namaqualand Region, South Africa

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Abstract

In this study, the hydrochemical characteristic changes of open-pit groundwater (OPGW) near a closed metalliferous mine proposed for drinking and irrigation usage were investigated. Water samples from an OPGW in O’Kiep were collected in April (dry season) and August (wet season), 2017. Data analysis methods, such as the coefficient of variation, correlation coefficient, piper trilinear plot analysis and sodium adsorption ratio (SAR) among others were used to assess of the seasonal variation in the OPGW quality. The hydrochemical characteristics of the OPGW were also compared with drinking water guidelines. Based on the results, it was evident that the OPGW quality varied seasonally. The most abundant cation and anions were Ca^{2+} and SO_4^{2-} , with recorded concentrations of 631 and 6020 mg/L, (dry season); 541 and 4450 mg/L (wet season), respectively. The OPGW was relatively rich in $\text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ during the dry season; however, these cations and anions were reduced during the wet season with Cl^- and Na^+ subsequently increasing. PHREEQC indicated that cation exchanges played a significant role in the OPGW chemistry with Sb and Ca appearing to be the minerals with the highest precipitation potential followed by Cu_7S_4 and Blaubleil , respectively. Covellite , CdSe_2 and NiSe were likely to be in equilibrium while Ca_3Sb_2 will remain in a dissolution state. Furthermore, the seasonal fluctuation in the OPGW quality characteristics was attributed to the water table level fluctuations and the water quality did not satisfy the guidelines stipulated by the South African National Standard, SANS241-1 (2015) and World Health Organisation, WHO (2011). The trilinear piper plot classified the OPGW into three types: $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^- \text{-SO}_4^{2-}$; $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-F}^-$; and $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-SO}_4^{2-}$. Overall, the SAR values were within the permissible levels for irrigation purposes; however, long-term use of the OPGW might be detrimental for plant growth.

Keywords Arid region · Closed metalliferous mine · Hydrochemical characteristics · Groundwater · O’Kiep

Introduction

In South Africa (SA), the vicinity of operating mines to water sources culminates in the contamination of such sources, including groundwater due to the exposure of different geochemical profiles of underground aquifers by elements mined. The variance in the hydrochemical profile of groundwater differs for each location, thus depends on climatic and seasonal changes, including the geological profile of the area (Jonch-Clausen 2004; DWA 2004). Mining activity can also change the hydrochemical profile of groundwater. Contaminated groundwater has been one of the challenges faced by communities in SA as groundwater is considered as one of the primary water resources for developmental activities, however, its quality is adversely affected or degraded as a result of anthropogenic activities

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that introduce pollutants into the groundwater. Overall, groundwater contamination is usually irreversible (Rajendran et al. 2019; Abdelgawad 2005).

Environmental challenges arising from mining activities are receiving increasing attention in SA generally; however, less so in small former copper mining areas, such as O’Kiep, which was considered in the eighteenth century to be the richest copper mining area in the world (Cairncross 2004). Currently, this town is experiencing various challenges, such as poor drinking water quality. In O’Kiep, the mining of copper left a legacy of metalliferous waste, such as tailings, waste rock and contaminated soils within the vicinity of this town. Generally, such mining activities are known to pollute both the immediate environment and ground and/or surface water resources. This can culminate in water shortages, even if water is available from various sources (Singh and Kamal 2015) it might be contaminated.

Groundwater is a key component of the water resources of SA. As such, it can provide much of the water required for households, especially since the country’s surface water resources are unevenly distributed and cannot cope with growing demand (Bredenhann and Braune 2000). In a report of surface and groundwater assessment in Namaqualand, an area which includes O’Kiep, the levels of several contaminants in the groundwater from some boreholes were higher than the SANS Class II drinking water limits and therefore the water was not suitable for human consumption (Holmes 1995). Additionally, the analysis also indicated that, the groundwater quality exceeded the recommended values for livestock use, as set out in South African water quality guidelines for agricultural use and livestock (DWA 1996, Holmes 1995), with mining activity suspected to be a source of the contamination.

The geochemistry of the minerals mined in the O’Kiep area is such that sulphidic ores are the dominant minerals in the copper-rich ore body of the area (Faris et al. 2017). Copper sulphide ores that are common in the O’Kiep area are bornite (Cu_5FeS_4), chalcopyrite (CuFeS_2), chalcocite (Cu_2S), digenite (Cu_6S_5), enargite (Cu_3AsS_4) and pyrite (FeS_2) (Hangone et al. 2005). These are the primary constituents in the ore body that facilitate acid rock drainage, sulphide geological material oxidation and the transportation of potentially toxic elements (PTEs) by leaching (Fosso-Kankeu et al. 2015, 2017; Munyai et al. 2016). Dissolved minerals in the surface water can be transported and thus pollute groundwater when the water table is high. Sulphide containing ores are known to produce acid when exposed to oxygen and water (Plumlee 1999). The oxidation of pyrite and copper sulphide ores in tailings and mine dumps is due to weathering as described by Antonijević et al. (2008). Generally, such weathering can enhance the mobility of PTE species which can contaminate groundwater.

The national state on water resources report by the DWA (2011–2012) on climatic conditions, indicated a reduction in rainfall and an increase in evaporation due to higher temperatures that impacted on the SA’s scarce water resources. Additionally, the groundwater in O’Kiep is highly susceptible to high evaporation rates. Natural factors that could influence changes in the quality of the groundwater in O’Kiep include the host rock, precipitation, evapotranspiration and acid rock drainage (ARD) formation (Van Dyk et al. 2008). Under excessive evaporative conditions, groundwater salinity displays a cumulative tendency to increase (Abiye and Leshomo 2013). Furthermore, groundwater arid and semi-arid environments are subjected to periodic salinisation due to high evaporation rates and low rainfall (Nakwafila 2015). The understanding of groundwater hydrochemical characteristics is a vital factor in determining its safety for use in domestic and agricultural activities. Therefore, it was necessary to investigate the seasonal variation of the quality of an open-pit groundwater (OPGW) near a closed metalliferous mine. Earlier studies by Erdogan et al. (2017), carried out in this area, evaluated the hydrochemical characteristics of the OPGW quality. However, these studies did not attempt to assess the seasonal variation in the OPGW quality. Therefore, the objective of this study was to assess the seasonal variation of the OPGW quality, and to determine its suitability for drinking and irrigation purposes.

Materials and methods

Site description

O’Kiep is situated in Namaqualand, Northern Cape Province of South Africa (Cairncross 2004) with coordinates [29° 35′ 45″ S 17° 52′ 51″ E]. This town is 38.63 km² in size with a reported population of approximately 6300 people in 2011 and is approximately 570 km from Cape Town. O’Kiep is characterised by an arid climate with no perennial river systems. The Lower Orange River (LOR) is the only perennial river, located some 150 km east of O’Kiep and it is a major source of piped drinking water supply for agricultural, domestic and industrial use for the town. The geometry of the aquifer systems in O’Kiep has been largely influenced by the underlying geology of metamorphic rocks, such as granites (Pietersen et al. 2009). The groundwater in the so-called Namaqualand aquifer occurs in the alluvial and crystalline basement rocks (Adams et al. 2003), with the Spektakel aquifer previously having supplied water to O’Kiep, Nababeep and Springbok. However, this was replaced by the water supply scheme from the LOR (Nuclear 2006) due to suspected contamination of the aquifer attributed to long-term copper mining and poor groundwater management practices. The hydrochemistry of groundwater in

Namaqualand aquifer indicates dissimilar composition due to the ensuing complex geochemical processes as the chemistry is being controlled primarily by dissolution, redox reactions and mixing (Abiye and Leshomo 2013). A further source of water is an open-pit situated 1.1 km downstream from the closed O’Kiep metalliferous mine, which is filled with water.

Sample collection

Prior to the sample collection, permission was granted by the O’Kiep Copper Company and Namakhoi municipality for the purposes of this study. Samples ($n = 10$) in duplicate were collected from the open-pit [29° 35’ 55.1” S 17° 52’ 47.6” E] (144 m width, 10 m depth), on the 5th of April 2017, a dry season (average temperature of 37 °C) and on the 8th of August 2017, a wet season (average temperature of 16 °C) with a minimal rainfall occurring in the area on the day of sampling (Accuweather 2017). The samples were collected between 7 and 11 a.m. for both seasons. The sampling points were randomly selected due to soil erosion and restricted access to the open-pit. Multi-parameter

instruments were calibrated prior to field measurement usage according to the national field water measurement standards (Gibs and Wilde 2007; Wilde and Radtke 1998), with polypropylene sample bottles (500 mL) being used for sample collection. The sampling bottles were thoroughly cleaned and rinsed in dilute 0.5 M HCL, prior to rinsing with sterile deionized water. The bottles were air-dried and stored closed to prevent pollution prior to sample collection. Samples were collected around the open-pit in duplicate at depths between 1 and 9.5 m (dry season) and 1 and 11 m (wet season) using a HydraSleeve™ “No-Purge” groundwater sampler according to the method described by Trick et al. (2008), with GPS coordinates being recorded at the sampling points as shown in Fig. 1, which indicates the sampling area, and potential sources of contaminants, i.e. stockpiled metalliferous waste and tailings storage facility.

During sampling, the following physical parameters were quantified onsite, using an EXSTIK II® EC500 and an EXSTIK II® CA895, for dissolved oxygen (DO): pH, temperature, electrical conductivity (EC), redox potential (ORP), salinity and total dissolved solids (TDS). The instruments were calibrated prior to sampling using standard procedures

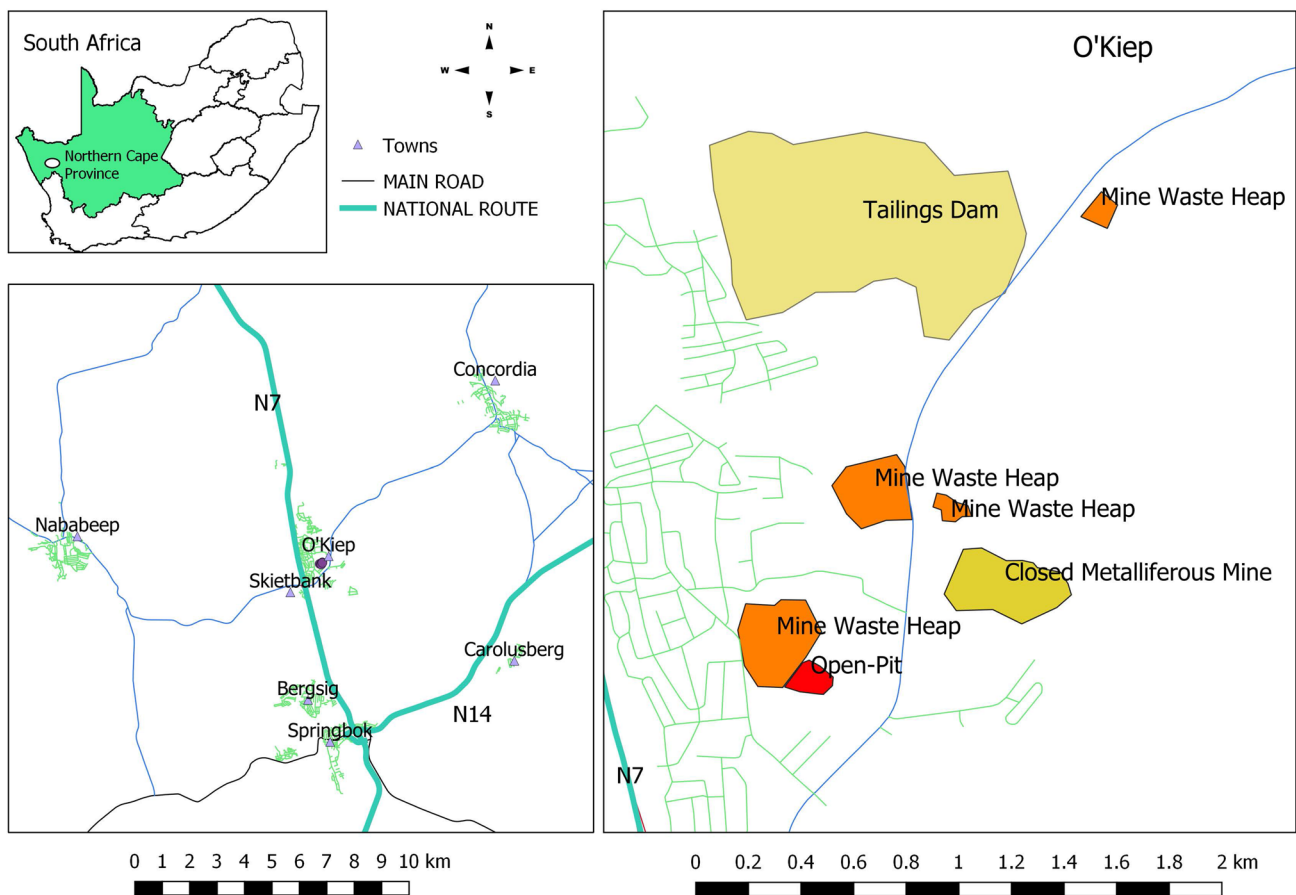


Fig. 1 XXX

as described by Shah and Mjalli (2014). The temperature was measured in situ to minimise atmospheric variations according to the method described by Weaver et al. (2007a) and Sundaram et al. (2009). Samples were also filtered through a 0.45- μm cellulose membrane filter, using a hand-vacuum pump, into polypropylene sampling bottles (Ball et al. 1999, APHA 2005). The unfiltered 100 mL per sample were digested with technical grade nitric acid (0.2 M). Unless otherwise stated, all reagents used, were of analytical grade, while standardised methods of analysis were used (APHA 2005).

All samples were stored in cooler boxes with ice to ensure preservation during transportation to the laboratory thereby further analyses were performed. All samples were analysed without dilution. Analyses performed included quantification of anions, cations, PTEs and chemical oxygen demand, using UV–Vis spectrophotometer, high-performance liquid chromatography (HPLC), inductively coupled plasma coupled either with a mass spectrometer (ICP-MS) or an optical emission spectrometer (ICP-OES) at an external South African National Accreditation System (SANAS) accredited laboratory.

Data analysis

Multivariate statistical analysis using Microsoft Office Excel 2016[®], was used for the assessment of the OPGW quality focusing on the coefficient of variation (CV) (Stanković et al. 2015), correlation analysis (CA) and the trilinear piper plot.

The coefficient of variation and correlation analysis

The quality variability of the OPGW can be measured by determining fluctuations in the water table and can be expressed as a coefficient of variation (Stanković et al. 2015). The contributing aquifer can have a dynamic range of groundwater levels as they discharge and recharge seasonally (Quevauviller et al. 2009). The CV was determined using Eq. (1) (Abdi 2010):

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100. \quad (1)$$

The first step prior to the multivariate statistical analyses is to reduce data sizes by eliminating the variables that do not provide important information of groundwater quality. Therefore, parameters indicating a < 5% CV were considered almost constant and thus excluded from the statistical analyses (Pacheco Castro et al. 2018; Güler et al. 2002).

CA is a bivariate technique used to define the degree of relation between two hydrochemical parameters. CA has been broadly used as an unbiased method for drawing

meaningful information in the analysis of water quality variation (Singh et al. 2005; Selvakumar et al. 2017).

Geochemical modelling

A thermodynamic model with a mathematical program was applied to determine ion interactions (Leonard and Pierre 2013). Dissolution–precipitation processes, saturation indices (SI) of some mineral phases were calculated with PHREEQC Version 3 software (US Geological Survey) that elucidate speciation and reaction mechanisms (Zhu and Anderson 2002; Parkhurst and Appelo 1999). Furthermore, speciation, solubility, reaction and inverse mass balance modelling were activated to complete the process. The MINTEQ.V4.DAT database was used for the ion interaction approach. The redox potential (pe) value was determined using a portable ORP instrument (Hi 98190). The Ag/AgCl electrode reference was used as a comparison with the hydrogen scale (Nordstrom and Wilde 2005). Additionally, a PHREEQC batch reaction model was used to perform irreversible and equilibrium reactions (see Eqs. 2 and 3).

$$Eh = \text{ORP} + E\Theta, \quad (2)$$

$$Pe = Eh \frac{\text{mv}}{59.2} \text{mV}. \quad (3)$$

Sodium adsorption ratio

The sodium adsorption ratio (SAR) is a measure of the suitability of water for irrigation purpose. The formula for calculating the sodium adsorption ratio is presented in Eq. (4) (Manoj et al. 2017):

$$SAR = \frac{\text{Na}^+}{1/2[\text{Ca}^{2+} + \text{Mg}^{2+}]} \quad (4)$$

Results and discussion

Table 1 presents the seasonal variation of the OPGW. The OPGW temperature showed a wide range of variation from an average of 23.0 °C (dry season) to 14.4 °C (wet season), which reflected a seasonal change in atmospheric air temperature. The pH values of OPGW samples during dry and wet season were slightly acidic, at pH 4.5–5.2 and 3.7–3.8, respectively. The pH values for the water sampled in both seasons were not within the permissible limit for drinking water according to SANS241-1 (2015) and WHO (2011). This includes the low average DO concentrations in both dry (0.9 mg/L) and wet season (0.1 mg/L) samples, indicative of the anaerobic conditions of the OPGW. A decrease in COD

Table 1 Physico-chemical characteristics of open-pit groundwater (OPGW) compared to water quality guidelines

Parameters	Units	Dry season (n=5)						Wet season (n=5)						Water quality guidelines		
		Min	Max	STDV.P	Average	CV (%)		Min	Max	STDV.P	Average	CV (%)	SANS 241:2015	WHO:2008		
<i>Chemistry parameters</i>																
Chemical oxygen demand (COD)	mg/L	14.6	88	28.2	53	53	14.6	15	0.0	14.6	0	-	-	4		
Alkalinity (CaCO ₃)	mg/L	10.0	10.0	0.0	10.0	0	10.0	10.0	0.0	10.0	0	-	-	-		
<i>Physical parameters</i>																
Colour	Pt-Co-true	10.0	23	5.2	12.6	41	10.0	10.0	0.0	10	0	<15	-	-		
Turbidity	NTU	502	4000	1504	1396	108	14.9	148	57	50	113	≤5	5	5		
pH at 25 °C	-	4.5	5.2	0.2	4.9	4	3.7	3.8	0.1	3.7	2	5-9.7	6.5-8.5	-		
Temperature	°C	19.2	24.7	2.0	23.0	9	14.1	14.3	0.1	14.2	1	-	-	-		
Electrical conductivity (EC)	mS/m	7380	9000	527	8202	6	6065	7005	399	6756	6	≤170	-	-		
Total dissolved solids (TDS)	mg/L	5145	6283	370	5717	6	3435	3640	81.4	3501	2	≤1200	500	-		
Dissolved oxygen (DO)	mg/L	0.4	1.2	0.3	0.9	30	0.1	0.1	0.0	0.1	0	-	5	-		
Salinity	Ppt	3.7	4.5	0.3	4.1	6	4.8	5.1	0.1	4.9	2	-	-	-		
redox (ORP)	mV	110	130	7.0	123	6	159	167	3.1	164	2	-	-	-		
<i>Cation and anion parameters</i>																
Calcium (Ca)	mg/L	544	631	29.6	600	5	533	541	3.1	536	1	-	-	-		
Sodium (Na)	mg/L	420	559	50.1	492.8	10	477	572	40.0	503	8	≤200	100	-		
Magnesium (Mg)	mg/L	434	683	85.1	544	16	475	505	12.6	483	3	400	-	-		
Potassium (K)	mg/L	29.2	42.8	4.5	34.9	13	31.3	33	0.4	31.9	1	-	-	-		
Fluoride (F ⁻)	mg/L	5.41	9.6	1.4	6.8	21	1.0	4.0	1.2	2.7	43	≤1.5	1.5	-		
Chloride (Cl ⁻)	mg/L	607	759	60.1	686.8	9	960	1080	45.6	1035	4	≤300	250	-		
Sulphate (SO ₄ ²⁻)	mg/L	4020	6020	665	4830	14	4240	4450	85.8	4303	2	≤500	200	-		
Ammonia (NH ₃)	mg/L	0.18	2.4	0.9	1.0	93	0.47	0.5	0.0	0.5	2	≤1.5	-	-		
Nitrate (N)	mg/L	10.0	10.0	0.0	10.0	0	0.5	0.5	0.0	0.5	0	≤0.9	45	-		
Ortho-phosphate (P)	mg/L	3.51	3.77	0.1	3.6	2	0.5	0.5	0.0	0.5	0	-	0.4	-		
<i>Elemental parameters</i>																
Aluminium (Al)	mg/L	8.4	76.7	24.5	38.8	63	7.5	8.0	0.19	7.7	3	≤300	-	-		
Antimony (Sb)	mg/L	0.02	0.02	0.0	0.02	0	0.01	0.02	0.004	0.018	25	≤20	-	-		
Arsenic (As)	mg/L	0.01	0.01	0.0	0.01	0	0.01	0.02	0.004	0.013	35	≤20	0.01	-		
Cadmium (Cd)	mg/L	0.06	0.08	0.01	0.07	10	0.0	0.1	0.01	0.0	41	≤3	0.003	-		
Chromium (Cr)	mg/L	0.04	0.16	0.05	0.08	57	0.0	0.0	0.01	0.0	33	≤50	-	-		
Cobalt (Co)	mg/L	1.43	1.64	0.07	1.54	5	1.8	1.8	0.02	1.8	1	-	-	-		
Copper (Cu)	mg/L	464	1130	252	628	40	440	453	5.2	447	1	≤2000	1.0	-		
Iron (Fe)	mg/L	28.8	214	77.8	79.5	98	0.4	0.8	0.1	0.6	18	≤2000	0.3	-		
Manganese (Mn)	mg/L	36.5	40.5	1.5	39.0	4	31.4	32.0	0.2	31.8	1	≤400	0.05	-		
Mercury (Hg)	mg/L	6.0	6.0	0.0	6.0	0	0.01	0.0	0.0	0.01	0	≤6	-	-		

Table 1 (continued)

Parameters	Units	Dry season (n = 5)					Wet season (n = 5)					Water quality guidelines		
		Min	Max	STDV.P	Average	CV (%)	Min	Max	STDV.P	Average	CV (%)	SANS 241:2015	WHO:2008	
		Nickel (Ni)	9.29	11.4	0.7	9.9	8	9.21	9.3	0.0	9.3	0	≤ 70	70
Selenium (Se)	0.04	0.04	0.0	0.04	0	0.04	0.04	0.0	0.04	0	≤ 40	40		
Vanadium (V)	0.01	0.15	0.06	0.06	98	0.01	0.01	0.0	0.01	0	≤ 200	-		
Zinc (Zn)	0.01	0.03	0.01	0.02	52	0.005	0.005	0.0	0.005	1	≤ 0.005	2		
Cyanide (CN ⁻)	0.14	0.39	0.08	0.30	28	0.034	0.083	0.02	0.049	41	≤ 200	-		

CV*: coefficient of variation

ranging from 53 to 15 mg/L for both seasons indicated low organic matter in the OPGW; thus, an insignificant organic matter contamination; albeit COD can also be reduced due to chemically induced chelating during thermal oxidation in slight acidic water (Osborne et al. 2009). Overall, the CODs were greater than the WHO (2011) water quality guideline value of 4.0 mg/L. Generally, DO has a significant effect upon groundwater quality since it regulates the solubility of many trace metals and limits the bacterial metabolism of organic compounds by aerobic bacteria. Some bacteria use DO as part of their metabolism in certain cases, facilitating the oxidation of ammonia, hydrogen sulphide, organic carbon and other reductants (Weaver et al. 2007b). The DO content also indicated changes in the redox state and microbial activity of the water samples (Pretorius et al. 2008) as ORP increased from 123.1 mV (dry season) to 164 mV (wet season).

The OPGW salinity was noticed to increase from 4.1 g/L (dry season) to 4.9 g/L (wet season). The OPGW salinity is a significant groundwater quality indicator, which is controlled by many factors such as aquifer mineralogy, and topography even mobility of PTEs into the water from the surface of the contaminated area as a result of mining activity (Praveena et al. 2011). Rabbani et al. (2010) also reported that saline water starts to infiltrate inland during the wet season, with Yan et al. (2015) concluding that groundwater salinity varies with the fluctuation of groundwater level. According to the Northern Cape Department of Environmental Affairs and Nature Conservation (Goegap Nature Reserve report 2018), most of the rainfall in O’Kiep varies between 100 and 300 mm per year; however during sampling in August 2017, only 2 mm of rain was recorded. Furthermore, the TDS and EC slightly decreased from 5717 mg/L and 8202 mS/m (dry season) to 3501 mg/L and 6756 mS/m (wet season), respectively. EC of the OPGW is a direct function of its TDS and indicates concentration of soluble salts in the groundwater (Harilal et al. 2004; Purandara et al. 2003). These values were not within the allowable limits by SANS241-1 (2015) and WHO (2011). The OPGW contained high dissolved solids content which may be caused by human activity (Ramakrishnaiah et al. 2009).

For different seasons, the groundwater turbidity varied from a maximum of 4000 NTU (dry season) to a minimum of 148 NTU (wet season). High turbidity values during the dry season were due to clay and silt-sized particles present at the edges of the open-pit. The turbidity values for both seasons were above the drinking water quality limit stipulated by SANS241-1 (2015). The causes of water turbidity are diverse; and in most cases, the suspended and dissolved solid particles contribute to high turbidity, with some particles being pneumatically transported into receiving water especially during the dry season. However, turbidity can also indicate the presence of dissolved hazardous PTEs and

the proliferation of microbial contaminants. The less turbid water (NTU 148) obtained during wet season could be an indication of aquifer recharge (Mativenga and Marnewick 2018). The CV for turbidity increases were from 108% (dry season) to 113% (wet season) with both seasons having a CV greater than 100%, an indication of variability (Ma et al. 2011). This was an indication that environmental alterations might critically affect the OPGW in this arid area. Similarly, an alkalinity of 10 mg/L for both seasons was observed, with sulphate reduction being hypothesised as contributory factor (Whitworth et al. 2014), which is also an indication of sustained microbial activity and slow weathering of non-carbonated rocks, such as the igneous granite and gneiss (Pretorius et al. 2008).

The ions concentration in the OPGW samples varied in both seasons. The most abundant cation and anions were Ca^{2+} and SO_4^{2-} . The high level of Ca^{2+} , Mg^{2+} and SO_4^{2-} concentration was associated with the oxidation and weathering of sulphide minerals, which may be due to dissolution of gypsum- and calcium-bearing minerals (Selvakumar et al. 2017). Similar results were obtained in a study of Abiye et al. (2018) through which hydrogeochemical parameters of the groundwater system in the Namaqualand region were studied. The relative ionic abundance in the OPGW at the O’Kiep copper mine area showed that the trend for cation availability in the following sequence $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{NH}_3$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{PO}_4^{3-}$ for anions. An increase in Na^+ , Cl^- , Ca^{2+} and SO_4^{2-} was an indication of the dissolution of quaternary sand, scree rubble and sandy soil deposits in which minerals, such as anhydrite, halite and gypsum occur.

The CV of the abundant Cl^- and SO_4^{2-} anions decreased during the wet season from 9 to 4% and from 14 to 2%, respectively. On the other hand, F^- had a lower variation in the dry season (21%) albeit higher in the wet season (43%). Fluoride is a major component of fluorite (CaF_2), an additional mineral in granites. Dissolution of such minerals can constitute a major source of F^- in groundwater (Edmunds and Shand 2009; Reddy et al. 2010). Additionally, more people in nearby areas in Namaqualand suffer from tooth decay, and decolouration assumed to be due to high concentration of F^- . The high F concentration is typical for groundwater in granitic aquifers (Abiye et al. 2018).

Al, Cr, Cd, Cu, Fe and Zn all decreased from dry season to wet season from 63 to 3%, 57 to 33%, 5 to 1%, 40 to 1%, 98 to 1% and 52 to 1%, respectively. However, the Sb, As, Cd and CN^- increased to 15, 35, 41 and 41%, respectively. This was attributed to natural seasonal groundwater table fluctuations (Rijal et al. 2010). When the OPGW pH is low, the higher the mobility of Sb, As, Cd and CN^- ; thus, mobilisation in the groundwater a phenomena linked to the geologic setting of the study area, which is further influenced

by the geochemistry of the mine waste, mine tailings which contaminates the immediate environment in the study area (Erdogan et al. 2017, 2018; Moncho et al. 2017). Additionally, geochemical processes controlled the mobilisation of Sb and As (Ramos et al. 2014). Aquifers in the Northern Cape, Namaqualand, are mostly assumed to be affected by natural conditions with only seasonal trends responsible for water level fluctuations. Depending on the aquifer type including rainfall can have a more significant influence on the groundwater quality (Adams et al. 2003; Van Dyk et al. 2008). Some aquifers are susceptible to contamination from surface sources. Fractured aquifers also allow rapid migration of contaminants via a preferred pathway, culminating in the potential to contaminate vast areas along the fracture network (Adams et al. 2004). The topography in this region is defined as a flat terrain with isolated mountains and hills. The observed hydraulic head and elevation data gathered from the hydrocensus indicate that the groundwater level in Namaqualand is related to its topography (Roets 2008; Ferreira et al. 2015). During the raining season, water can flow along the hydraulic gradient from the north-west to the south-east (Ferreira et al. 2015). The vegetation and flowers in this area bloom during the wet season, having adapted to this habitat with its alternating periods of exposure and inundation. From the results, it is observed that the maximum SAR value for the dry season was 22, while for the wet season it was 25, values which are within permissible levels for irrigation. However, as this groundwater is mildly acidic (pH = 3.7–5.2) with very high salinity and Na^+ concentration levels was determined to be influenced weathered overburden in this mining area, thus continuous use of such water may cause a poor physical soil environment. A high amount of Na^+ concentration in irrigation water can adjust the osmotic pressure in the root zone of some plants, which can result in limiting the amount of water taken in by the plant which will consequently hinder plant growth (Ouyang et al. 2014; Selvakumar et al. 2017).

The OPGW had a high sulphate concentration of 4830 mg/L for the dry season and 4303 mg/L for the wet season. Also, there were elevated concentrations of dissolved trace elements in the dry season, in particular, $\text{Cu} > \text{Fe} > \text{Al} > \text{Mn}$. It was also noted that the higher the water table would rise due seasonal fluctuation during the wet season, the lower the values of trace elements ($\text{Cu} > \text{Fe} > \text{Al} > \text{Mn}$) and turbidity (Rao 2006). However, the PTEs, such as Al, Sb, As, Cd, Cr, Co, Cu, Fe, Mn, Hg, N, Se, V, Zn and CN were all within ≤ 20 mg/L, a water quality guideline stipulated by SANS241-1 (2015), while As, Cu, Fe, Mn were above 0.01 mg/L and not being within limits by the WHO (2011). The presence of As and Fe is an indication of oxidation of arsenic sulphides, such as arsenopyrite (FeAsS) and pyrite (FeS_2) in the groundwater (Zheng et al. 2004) and As also mobilises under anaerobic conditions

as influenced by low DO concentrations (Tomlinson et al. 2017). However, it can be seen in Table 1 that low concentration of arsenic (As) was 0.01 mg/L, albeit the nitrate concentration was 10 mg/L and DO of 0.9 mg/L (dry season) and 0.1 mg/L (wet season) were also observed. Additionally, a DO level less than 1.0 mg/L is an indication of anaerobic conditions in the OPGW (Dinicola 2006). Additionally, in the study of Leshomo (2011), As was rarely detected in the groundwater of Namaqualand area. Similarly, no uranium was detected in the OPGW for both seasons which could be due to the geology of the O’Kiep which comprise of granite (Clifford and Barton 2012). Moreover, uranium concentrations in groundwater in granite geological formations results in spatial distributions which are preferentially localized (Cho and Choo 2019). Similar results were also obtained in a Jurassic granite in Korea with low concentration of uranium (Cho and Choo 2019). Lowest uranium concentrations were also observed in groundwater characterized by iron and sulfate reducing conditions (Riedel and Kübeck 2018). These observation are further supported by the fact that the O’Kiep geology consists of thick sheet of granite gneiss up to 1500 m thick (Clifford and Barton 2012). Some physical parameters, cations, anions and trace elements, such as pH, TDS, Na^+ , Mg^{2+} , K^+ , F^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , Al, Cu, Fe, Mn and Zn would be much higher than those of natural groundwater associated geological formations, with the physical parameters being hypothesised to be due to leaching of elements from the surrounding waste rock mine dumps and tailings. Further study is; however, needed to better understand the mobility mechanism and sources of these PTEs occurring in various concentrations in the OPGW (Larkins et al. 2018). The chloride observed is a broadly distributed component in all types and forms of rocks (Pretorius et al. 2008). Its affinity towards sodium is high, with Na^+ and Cl^- concentrations increasing during the wet season from an average of 493 to 503 mg/L and from 687 to 1035 mg/L, respectively. According to Jeevanandam et al. (2007), the active dissolution of the halite in the OPGW was assumed to be the main cause of the high Na^+ and Cl^- during the wet season. Soil permeability and porosity also have a key role in chloride concentration development (Ramakrishnaiah et al. 2009).

Classification of the groundwater in O’Kiep

The trilinear piper diagrams of the OPGW samples for both seasons are shown in Fig. 2. Groundwater in granitic rock is normally classified as Na–(Ca)–Cl water-type and it is possibly controlled by mixing processes occurring between higher salinity groundwater Na–(Ca)–Cl water-type and low salinity groundwater (Na–(Ca)– HCO_3) water-type in the sedimentary rocks (Iwatsuki et al. 2005). Namaqualand experiences excessive evaporative conditions due to its aridity,

as such the hydrochemical parameters increased, with the overall salinity being observed to be elevated. These changes in the groundwater quality might be primarily through parent rock weathering, dissolution and anthropogenic sources. It was presumed that natural geological sources could be the cause for the groundwater quality deterioration in the area, which is further driven by climatic changes (Abiye and Leshomo 2013). In the lower right of both triangles, for the dry and wet season, all samples show SO_4^{2-} contents making up to 80% of the total anion load, indicating mixed water, without Ca^{2+} and Mg^{2+} cations exceeding 50% concentrations. When the concentrations of the ions were evaluated, it could be observed that the OPGW was relatively rich in $\text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ during the dry season. Additionally, an increase in Na^+ is likely to be attributed to silicate weathering (Brindha et al. 2017). An increase in Cl^- concentrations indicated an anthropogenic effect or flow of water into a nearby aquifer (Kumar et al. 2006).

The groundwater has a distinct Na–Cl character, mainly due to the geochemical composition of the crystalline rocks and alluvium from the Namaqua Metamorphic Complex (Titus 2002; Van Wyk et al. 2012; Braune and Xu 2010; Xu and Braune 2009) which primarily hosts groundwater in the study area. The Na–Cl dominant rainfall, dissolution and leaching of evaporates can further augment the salinity of the groundwater (Van Wyk et al. 2012). The hydrochemistry of the area indicates dissimilar groundwater composition due to complex geochemical processes thereby groundwater flow takes place and the chemistry is controlled primarily by redox reactions, dissolution and mixing processes. Under excessive evaporative conditions due to climatic aridity, groundwater salinity increases (Abiye and Leshomo 2013). Anions Cl^- and SO_4^{2-} dominated the OPGW composition, a phenomena attributable to gypsum and pyrite oxidation including halite dissolution which was reported by Raith et al. (2003) in this area. These processes that might control the ion enrichment are dissolution, redox, evaporation and the residence time, which promote water–rock interaction. Additionally, the study area, generally, has poor groundwater quality due to geogenic sources of chemical constituents; especially, PTEs (Erdogan et al. 2017; Abiye and Leshomo 2013). The chemical composition of the OPGW indicated the dominance of the Na^+ and Cl^- ions resulting in a Na–Cl water type and similar results were obtained by Nakwafila (2015). Cation exchange for both dry and wet season may account for a reduction in the Na^+ concentration, and halite dissolution may account for high concentration of Cl^- (Edet and Okereke 2002; Coyte et al. 2019). The OPGW is mostly classified into three types: (Ca^{2+} – Mg^{2+} – Cl^- – SO_4^{2-}); (Ca^{2+} – Mg^{2+} – F^-) and (Ca^{2+} – Mg^{2+} – SO_4^{2-}). The presence of these waters is due to the geology of O’Kiep and rock-forming feldspars comprising of anorthosite, which contains amphibole (Ca-bearing) (Clifford and Barton 2012). The

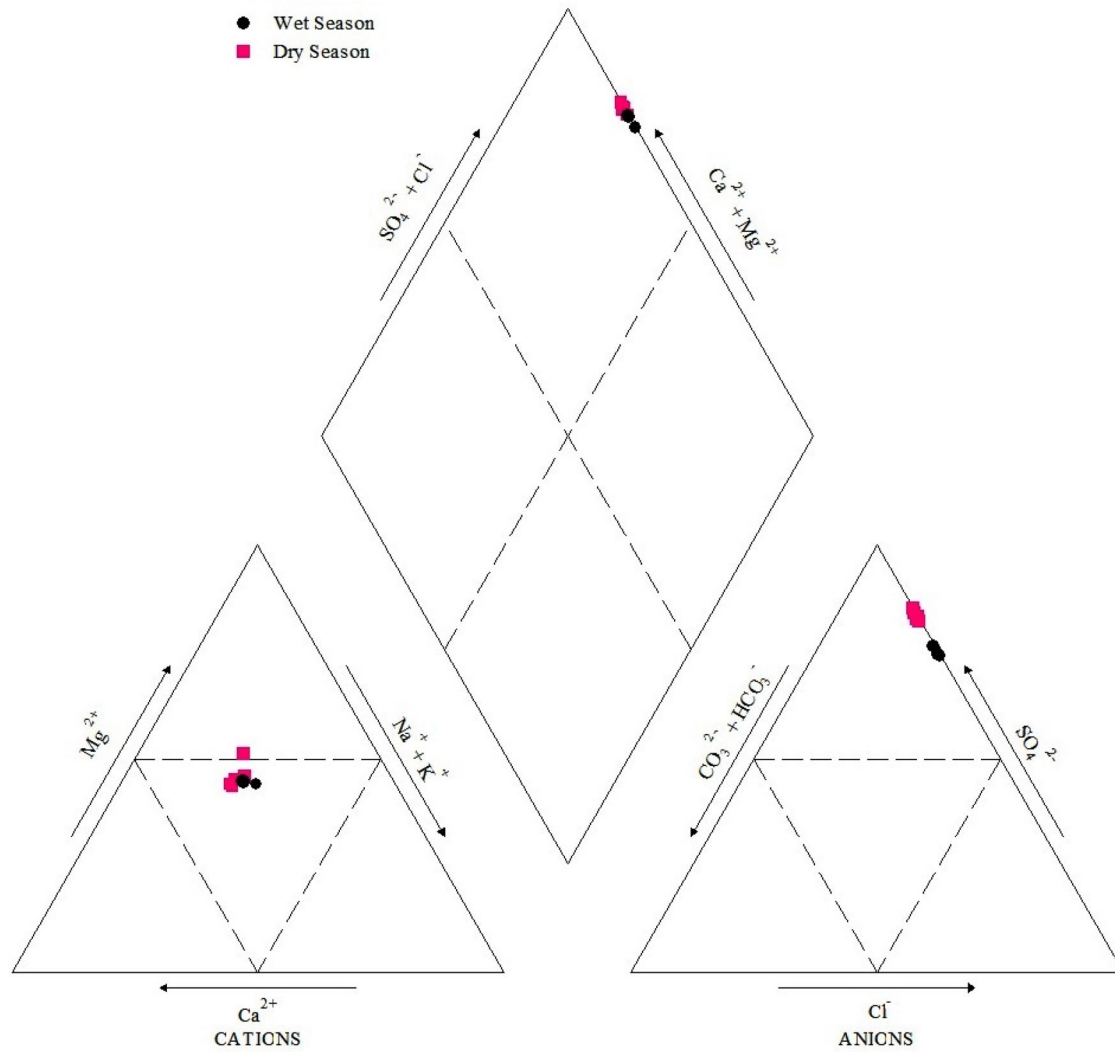


Fig. 2 Piper plot for both dry and wet seasons

Ca²⁺–SO₄²⁻ type represents effects of ARD and sulphide minerals dissolution (Lee et al. 2005).

The geochemical modelling performed with PHREEQC hydrogeochemical modelling software indicated that the cation exchange plays a significant role in controlling the OPGW chemistry. Additionally, the data generated suggested that a number of geochemical factors are influential, i.e. temperature and pH. Figure 3 enlists minerals that are partially in equilibrium and likely to precipitate during the contact between species. Chalcocite, CuSe, Anilite and Cu₃Se₂ appeared to be the minerals with the greatest chance of precipitation followed by Mn₂Sb and AlSb, respectively. Cu₃Se₂, FeSe₂ and HgSb had values greater than 10, whereas gypsum was likely to remain in equilibrium. Furthermore, Cu₃Se₂ is the most saturated and will likely lead to precipitation. MnHPO₄ is labelled as the least saturated entity and has a smaller chance to precipitate than the others. Chalcocite is

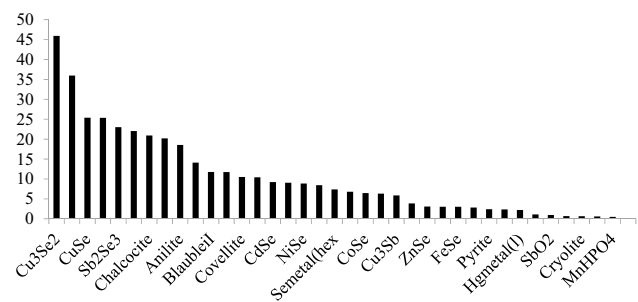


Fig. 3 The graph represents the mineral phases that could potentially precipitate during contact between species

known to contain the highest copper content (Beale 1985) and has a factor above 20. This translates to high copper deposits according to the model. High values do not always

ensure precipitation and are highly dependent on the reaction of the mineral (Bosire et al. 2018). While several other minerals, such as halite will remain in a dissolution state (S1: Erdogan et al. 2019).

The temporal variations in hydrochemical characteristics corresponded well with fluctuations sampling locations. Interestingly, the OPGW sampling was < 10 m sample depth that the chemical evolution would be driven in part by biogeochemical reactions and evapoconcentration and rock–water interactions (Mladenov et al. 2014). Sample depth showed no significant seasonal variation during the monitoring period, implying that temporal variations in hydrochemical characteristics in the OPGW were affected by a different patterns, i.e. combined control by internal sources and surface contributions (Shen et al. 2019). The hydrochemical characteristics in both seasons (< 10 m) showed insignificant seasonal variation, and any change in hydrochemical characteristics was inferred as being associated with anthropogenic activities.

Evaluation of the groundwater quality in O’Kiep

Ionic ratios of the open-pit groundwater are shown in Table 2. Hydrochemical indices assess the salinity and origin of the groundwater in the study area. Composition relations among dissolved species can reveal the source of solutes and the processes that generated the observed groundwater composition. Since Na, Ca, Cl, K, Mg, SO₄ were predominant ions in the OPGW, an analysis was made of stoichiometric relations that could account for the relative amounts of these ions. The average Na/Cl ratios for both dry and wet seasons were approximately 0.7 and 0.5, respectively, which is an indication of an alluvial aquifer since the ratio is less than 1 (Fisher and Mullican 1997). Overall, Mg/Ca, Mg/Ca, Na/Ca, Ca/Cl, K/Cl and Ca/SO₄ ratios were all less than 2.0. According to the interpretation of these indices, the groundwater in the study appears to be slightly of inland origin, because groundwater under marine influence would have values of approximately 5 (Morrel et al. 1986). An exception whereby other processes such as cationic exchange intervene would then contribute to values of less than 4

(Nwankwoala and Udom 2011). Ratios of Na/Ca, indicating cation exchange reaction can show some mixed behaviour, but would mostly decrease with decreasing TDS during the wet season while an increase would be observed during the dry season, a good indicator revealing the salinization process in an aquifer (Nwankwoala and Udom 2011; Edet and Okereke 2002).

Significance of the observed potentially toxic elements

The correlation coefficients among various OPGW quality parameters were calculated and the values are given in Tables 3 and 4. The resultant CA illustrated that COD showed a good negative correlation (− 1.0) with pH and temperature, and a positive correlation (+ 1.0) with EC, DO and ORP. The COD also showed a medium to weak correlation with turbidity, TDS and salinity. A significant positive correlation of SO₄^{2−} was noticed with Na⁺, Mg²⁺ and K⁺; EC and TDS had good correlation between salinity and DO in the dry season. The good correlation of Ca²⁺, Mg²⁺, Cl[−] and PTEs (except Fe) with SO₄^{2−} indicated that most of the ions were involved in hydrochemical reactions and seasonal changes of groundwater in O’Kiep, which indicated a common origin for these ions (Sahraei Parizi and Samani 2013). The groundwater mineralisation is predominantly related to these components (Shorieh et al. 2015). Such a correlation was obvious as EC is normally a function of dissolved ionic species in groundwater (Appelo and Postma 2004). The COD and DO did not show any significant relationship with any of the tested parameters during the wet season. The Cl[−] also showed a significant positive relationship with Na⁺, Mg²⁺ and K⁺. The turbidity had good positive correlation with pH, TDS, salinity and ORP during the wet season. In the present study, the significant correlations were observed among various metal pairs: Cd–Al, Cr–Al, Cu–Al, Fe–Al, Mn–Al, Zn–Al and CN–Al in the dry season, and between Ni–Al, Zn–Al, Mn–Al, CN–Al, Ni–Mn, Zn–Mn, Zn–Ni, CN–Zn, CN–Ni, C–Co in the wet season. The correlation between metal pairs indicated the existence of a common source of origin for these PTEs, or mutual

Table 2 Ionic ratios of the open-pit groundwater

Units	Dry season (n=5)			Wet season (n=5)		
	Min	Max	Average	Min	Max	Average
CaCO ₃ /Cl	0.02	0.01	0.01	0.01	0.01	0.01
Mg/Ca	0.80	1.08	0.91	0.89	0.93	0.90
Na/Ca	0.77	0.89	0.82	0.89	1.06	0.94
Na/Cl	0.69	0.74	0.72	0.50	0.53	0.49
Ca/Cl	0.90	0.83	0.87	0.56	0.50	0.52
K/Cl	0.05	0.06	0.05	0.03	0.03	0.03
Ca/SO ₄	0.14	0.10	0.12	0.13	0.12	0.12

Table 3 Correlation coefficient (*R*) for different parameters during dry season (*n* = 5) in the open-pit groundwater OPGW) in O’Kiep

Chemistry parameters	COD	Colour	Turbidity	pH	Temperature	EC	TDS	DO	Salinity	ORP
COD	1									
Colour	0.6	1								
Turbidity	0.6	0.6	1							
pH at 25 °C	− 1.0	− 0.2	− 0.8	1						
Temperature	− 1.0	0.1	− 0.7	0.9	1					
EC	1.0	0.2	− 0.5	0.4	0.7	1				
TDS	0.3	0.2	− 0.5	0.4	0.7	1.0	1			
DO	1.0	0.4	− 0.5	0.6	0.9	0.8	0.8	1		
Salinity	0.4	0.2	− 0.5	0.4	0.7	1.0	1.0	0.7	1	
Redox (ORP)	1.0	0.5	− 0.5	− 0.8	− 0.5	− 0.2	− 0.2	− 0.1	1.0	1
Cation and anion parameters	Ca ⁺	Na ⁺	Mg ²⁺	K ⁺	F ⁺	Cl [−]	SO ₄ ^{2−}	NH ₃	P	
Calcium (Ca)	1									
Sodium (Na)	0.7	1								
Magnesium (Mg)	0.5	1.0	1							
Potassium (K)	0.5	0.7	1.0	1						
Fluoride (F [−])	0.3	− 0.2	− 0.2	− 0.1	1					
Chloride (Cl [−])	0.6	0.9	0.9	0.8	− 0.1	1				
Sulphate (SO ₄ ^{2−})	0.5	0.7	1.0	1.0	− 0.1	0.8	1			
Ammonia (NH ₃)	0.1	0.0	0.5	0.6	0.4	0.3	0.6	1		
Ortho-phosphate (P)	− 0.1	0.5	0.4	0.4	− 0.2	0.7	0.3	0.2	1	
Elemental parameters	Al	Cd	Cr	Co	Cu	Fe	Mn	Ni	Zn	CN
Aluminium (Al)	1									
Cadmium (Cd)	0.9	1								
Chromium (Cr)	1.0	1.0	1							
Cobalt (Co)	0.6	0.5	0.2	1						
Copper (Cu)	0.8	1.0	1.0	0.3	1					
Iron (Fe)	1.0	1.0	− 0.2	0.2	1.0	1				
Manganese (Mn)	0.8	− 0.1	0.5	1.0	0.5	0.6	1			
Nickel (Ni)	1.0	1.0	1.0	0.4	1.0	1.0	0.6	1		
Zinc (Zn)	1.0	0.0	− 0.1	0.0	− 0.2	− 0.3	0.0	− 0.1	1	
Cyanide (CN)	0.9	0.4	0.4	0.2	0.6	0.6	0.3	0.5	− 0.9	1

Bold indicates statistically significant positive correlations

concentration dependence of the metals (Chabukdhara et al. 2017) in the OPGW. Such relationships of various physical parameters and metallic ions are expected due to several hydrochemical reactions, such as ion exchange and oxidation–reduction in a groundwater aquifer system (Chabukdhara et al. 2017).

Conclusion

This study assessed the seasonal variation of the OPGW quality near a closed metalliferous mine in O’Kiep (South Africa) and to determine its suitability for drinking and irrigation purposes. It was shown that changes in seasons have an influence on the hydrochemical properties of the

OPGW as evidenced by the low DO and COD concentration in both seasons showing prevailing anoxic conditions and deficiency of organic matter in the OPGW. Furthermore, result also indicated that the groundwater was slightly acidic, with high salinity during both the dry and wet season; albeit SAR both seasons showed that the OPGW was suitable for irrigation purpose; however, long-term use may cause damage to the soil. This was also further confirmed by a Mg/Ca ratio of less than 1.5. The PHREEQC suggested that the cation exchange played a significant role in controlling the OPGW chemistry with antimony and calcium appearing to be the minerals with the greatest chance of precipitation followed by Mn₂Sb and AlSb, respectively. The results of the present study provide information that can be useful for water resource management in the O’Kiep area; particularly,

Table 4 Correlation coefficient (*R*) for different parameters during wet season (*n*=5) in the open-pit groundwater OPGW) in O’Kiep

Chemistry parameters	Turbidity	pH	Temperature	EC	TDS	Salinity	ORP			
Turbidity	1									
pH at 25 °C	0.9	1								
Temperature	0.2	0.5	1							
EC	− 1.0	− 0.9	− 0.2	1						
TDS	1.0	0.9	0.0	− 1.0	1					
Salinity	1.0	0.9	0.1	− 1.0	1.0	1				
Redox (ORP)	1.0	− 0.8	− 0.1	0.9	− 1.0	1.0	1			
Cation and anion parameters	Ca ⁺	Na ⁺	Mg ²⁺	K ⁺	F ⁺	Cl [−]	SO ₄ ^{2−}	NH ₃		
Calcium (Ca)	1									
Sodium (Na)	− 0.2	1								
Magnesium (Mg)	− 0.4	1.0	1							
Potassium (K)	0.0	0.9	0.9	1						
Fluoride (F [−])	0.2	− 0.8	− 0.8	− 0.5	1					
Chloride (Cl [−])	0.1	0.1	0.1	0.5	0.5	1				
Sulphate (SO ₄ ^{2−})	− 0.2	1.0	1.0	0.9	− 0.8	0.1	1			
Ammonia (NH ₃)	− 0.3	0.1	0.2	− 0.3	− 0.7	− 1.0	0.1	1		
Elemental parameters	Al	Cd	Cr	Co	Cu	Fe	Mn	Ni	Zn	CN
Aluminium (Al)	1									
Cadmium (Cd)	− 0.6	1								
Chromium (Cr)	0.3	− 0.4	1							
Cobalt (Co)	0.7	− 0.1	− 0.5	1						
Copper (Cu)	− 0.1	0.3	− 1.0	0.6	1					
Iron (Fe)	− 0.5	0.2	− 0.1	0.1	0.8	1				
Manganese (Mn)	0.9	0.1	0.6	0.3	− 0.5	− 0.6	1			
Nickel (Ni)	1.0	− 0.7	0.2	0.7	0.0	− 0.3	0.9	1		
Zinc (Zn)	1.0	− 0.6	0.4	0.6	− 0.2	− 0.6	0.9	0.9	1	
Cyanide (CN)	0.9	− 0.7	− 0.1	0.8	0.2	0.0	0.7	1.0	0.8	1

Bold indicates statistically significant positive correlations

with respect to biodiversity changes due to anthropogenic effects. Based on these results, a water treatment system is recommended as a remedial measure for the contaminated OPGW in O’Kiep.

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