

# Geochemical Modelling Data of Groundwater in the O’Kiep, Namaqualand Region, South Africa – 2013 to 2019: A Case of Evidenced Contamination by Historical Mining Activity

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**Abstract** — The integration of hydrogeochemical characteristics techniques and geochemical modelling were used to identify the significant factors governing groundwater hydrogeochemical evolution in the Namaqualand. The groundwater was classified into four sets namely: Ca – Mg – HCO<sub>3</sub>, Na – K – HCO<sub>3</sub>, Na – K – Cl – SO<sub>4</sub>, and Ca – Mg – Cl – SO<sub>4</sub> between the periods of 2013 and 2019. The geochemical model PHREEQC suggests some geochemical reactions and mineral phases being responsible for the evolution of the groundwater chemistry and indicating that the groundwater hydrogeochemical evolution is mainly controlled by carbonate mineral dissolutions, cation exchange, precipitation and weathering. The increase in SO<sub>4</sub><sup>-</sup> concentration in the period of 2019 in groundwater was most likely due to sulfide-mineral oxidation. The contributions of anthropogenic sources were associated with the closed metalliferous mine, metalliferous solid waste, and acid rock drainage; it is predicted that the risk of potentially toxic elements in the study area will probably increase in groundwater in a long-term. The accumulation of SO<sub>4</sub><sup>-</sup> in the groundwater maybe due to the arid climate of the area. The groundwater of O’Kiep has been exposed to the progressive deterioration of water quality, with particularly significant increases in Na, Cl and SO<sub>4</sub>. This information would contribute to risk assessments and evaluation of remediation strategies. It is therefore anticipated that the groundwater contamination will continue to persist in the study area for many years if the mitigative strategies are not implemented.

**Keywords** — Arid region, closed metalliferous mine, groundwater evolution, O’Kiep, PHREEQC

## I. INTRODUCTION

Surface water is inadequate to meet the demand of drinking water in O’Kiep, due to the accumulative water demand by the

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increasing populace and urbanisation. On the other hand, it is unsafe to rely on the drinking water supply system (DWSS) in O’Kiep due to the possible bacterial contamination and regular interruptions in this area [1]. Furthermore, earlier studies suggest that potential acid rock drainage (ARD) formation is recognised as one of the environmental challenges associated with groundwater contamination in this former mining area as highlighted in [2]. Since groundwater is an essential resource for the community of O’Kiep, and could possibly be used in the near future for drinking and irrigation purposes, it’s monitoring is essential. Subsequently, some studies have been conducted in this area to determine the groundwater quality and its suitability for drinking and irrigation as discussed in [2], [3]. Although, soil acts as a natural filter, which removes and adsorbs the potentially toxic elements (PTEs), long-term release of ARD leads to the saturation of PTEs in the soil, with subsequent leachates sipping into the water table. Hence, it can also result in the reduction of filtration and adsorption capability of the soil and subsequently lead to deterioration of groundwater quality over time. Among many diverse contaminants, the presence of PTEs in groundwater is of major concern. Additionally, it has been reported that the ARD leaches into groundwater in O’Kiep. Overall, groundwater quality is influenced by the industrial activities, geology and climate conditions of an area. Furthermore, groundwater quality could be influenced by geochemical reactions such as dissolution, ion exchange, oxidation, precipitation in the aquifer whereby the groundwater is sourced [4], [5]. One of the tools that are normally used in hydrogeochemistry are the trilinear piper [6] and the Durov diagrams which evaluates the groundwater evolution while the latter reveals geochemical processes that could influence the groundwater genesis [4]. Hence, this part of the study aimed at determining the hydrogeochemical processes controlling the hydrogeochemical chemistry of the groundwater in O’Kiep and its evolution over time.

## II. MATERIALS AND METHODS

### A. Hydrogeochemical parameters

To determine the hydrogeochemical parameters of groundwater in O’Kiep, samples were collected from eight boreholes in the previous study of Erdogan, et al. [3], while

historical data were extracted from a study published by Abiye and Leshomo [7]. Most of the boreholes in the study area are associated with a fractured basement aquifer in the Namaqualand. The Namaqualand is situated in the South-Western region of South Africa, an arid region of the Northern Cape [8]. The method used for measurement of hydrogeochemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS) and ions are as described in the study of Abiye and Leshomo [7] for 2013 period and Erdogan, et al. [3] for 2019 period. These hydrogeochemical parameters were compared to drinking water quality guidelines as described by SANS241-1 [9] and WHO [10].

**B. Geochemical modelling**

PHREEQC v3, a computer program written in the C++ programming and developed by the US Geological Survey agency (<https://www.usgs.gov/software/phreeqc-version-3>), was used to perform an aqueous geochemical modelling that has capabilities to determine a saturation index (SI) and speciation determinations in a batch-type-reaction system [11], [12]. The interaction between the groundwater and rock mineralogy controls the geochemistry of the groundwater in specified study area [13]. Therefore, such an interaction was accounted for.

**C. Groundwater classification using trilinear piper and Durov diagrams**

To identify the different groundwater types for the area, the results of hydrogeochemical analyses were plotted on a trilinear piper diagram as presented in Fig. 1. The major ion concentrations of the groundwater data in the study area for the periods 2013 and 2019 were plotted on the confirmatory Durov diagram [14] as presented in Fig. 1b. Durov diagram improves the interpretation of the groundwater evolution and provides more information on the hydrogeochemical processes occurring in groundwater schemes such that it is easy to identify mixing of different water types, ion-exchange and reverse ion-exchange processes [15].

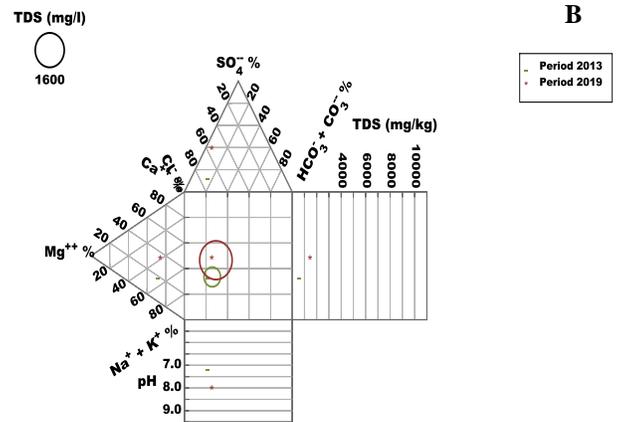


Fig. 1. Trilinear piper and Durov diagrams of the hydrogeochemical facies for groundwater classification.

**III. RESULTS AND DISCUSSION**

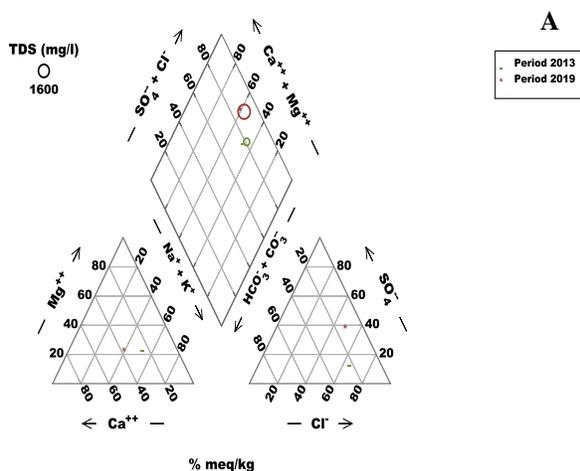
**A. Hydrogeochemical characteristics**

The high concentration values of standard deviation for these parameters display a high dispersion. This suggests that the groundwater hydrogeochemical characteristics showed a comprehensive spatial variation. The pH varied from 7.11 to 8.1, indicating that the groundwater was slightly alkaline, which was attributed to mineral sources such as carbonates in the groundwater [16]. The EC and TDS values of groundwater increased from 2.04 to 241 mS/cm and from 911 to 1793 mg/L, respectively. Additionally, the higher value of the standard deviation for EC (217 mS/cm) and TDS (1561 mg/L) suggests a great variability in the hydrogeochemical processes, which could be attributed to groundwater residence time, the heterogeneity of the nearby alluvial and crystalline basement of the aquifer [17] lithology and former mining activities especially in O’Kiep. In general, the abundant cations in groundwater were Ca, Mg and Na [16]. The concentration of Ca, Mg, and Na changed from 78.5 to 184 mg/L, from 51.5 to 67.3 mg/L and from 224 to 243 mg/L, respectively.

Carbonate dissolution is the key source of Ca and alkalinity in groundwater. With respect to anions, Cl dominated in the groundwater samples and the concentration changed from 447 to 470 mg/L followed by SO<sub>4</sub> from 121 to 455 mg/L. An increase of SO<sub>4</sub> with the increased in Cl could be due to the dissolution of soluble constituents such as halite and gypsum and halite as reported in [2]. On the other hand, the NO<sub>3</sub> and PO<sub>4</sub> decreased from 27.3 to 2.16 mg/L and from 1.41 to 0.5 mg/L, respectively. It was observed that most of the parameters including EC, TDS, Na and Cl were much higher than those obtained by [9] and [10].

**B. Groundwater classification**

The groundwater data for the periods 2013 and 2019 were described as chlorine type water, alkali and strong acid predominated and saline groundwater [16], [18]. The Namaqualand district is characterized by Na-Cl region and



widespread salt pans, which have significant role in governing the quality of groundwater salinity including increases, results which are similar to those obtained by Abiye, et al. [19]. The trilinear piper diagram presents the hydrogeochemical evolution of the groundwater during the studied period in the Namaqualand and substantiates the alterations amongst the four sets, namely: (Ca – Mg – HCO<sub>3</sub>), (Na – K – HCO<sub>3</sub>), (Na – K – Cl – SO<sub>4</sub>), and (Ca – Mg – Cl – SO<sub>4</sub>) types for both periods (2013 and 2019), (Fig. 1a). The groundwater evolved from low mineralized with EC of 2.04 mS/cm for 2013 period to progressive increase in salinity with EC of 241 mS/cm for 2019 period. Groundwater rich in Na and K represents 80% for both period 2013 and 2019. This was confirmed by the Durov diagram Fig. 1b, where the majority of groundwater were in ion exchange zone for the periods 2013 and 2019; while Ca was 21% for the period 2013 and 39% for 2019 period. However, groundwater dominant in Cl-SO<sub>4</sub>, producing a chlorine groundwater type represents 80% for the period of 2013 and 90% for 2019 period. Additionally, the Durov diagram shows that Cl ion is the main ion responsible for the increased salinity, even though the SO<sub>4</sub> ion is also significant in 2019. According to Leshomo [20] and as highlighted in the study by Erdogan, et al. [3], the salinity in the groundwater of Namaqualand is derived from halite dissolution and seawater mixing. For alkaline water with predominant Na–K–Cl–SO<sub>4</sub>, as strong acids (Cl and SO<sub>4</sub>), facies represent 90% for 2019 period. In general, ion-exchange process and weathering of rocks are mainly governing the groundwater hydrogeochemistry of Namaqualand. The data plots in trilinear piper diagram and Durov diagram revealed that cations were dominated by Na and K followed by Ca and Mg, while anions were dominated by Cl and SO<sub>4</sub> (Fig. 1b). The increased in SO<sub>4</sub> concentrations in 2019 period were hypothesized to originate from historical mining-associated activities due sulfide-mineral oxidation in the SMW and MTs [21].

### C. Geochemical modelling

In this part of the study, inverse geochemical model for the observed variations from the period 2013 to the period 2019 was performed, given that it is characteristic of groundwater hydrogeochemical evolution in the Namaqualand. A PHREEQC modelling software approach allows for the simulation and characterization of the hydrogeochemical processes influencing surface and groundwater qualities [22,23]. The composition of the groundwater contaminated by various PTEs can be used to predict reactive mineral mechanisms. Any variations observed between different datasets can determine the geological matrix interaction between significant anions and cations [24]. As PHREEQC determines the saturation index (SI) of various minerals in numerous mixtures and solutions; therefore, a positive SI indicates precipitation or supersaturation of secondary minerals and a negative SI indicates the dissolution or undersaturation of minerals; while an SI of ±0.5 indicates equilibrium conditions [25]. Fig. 2 represents the changes of the SI of particular phases.

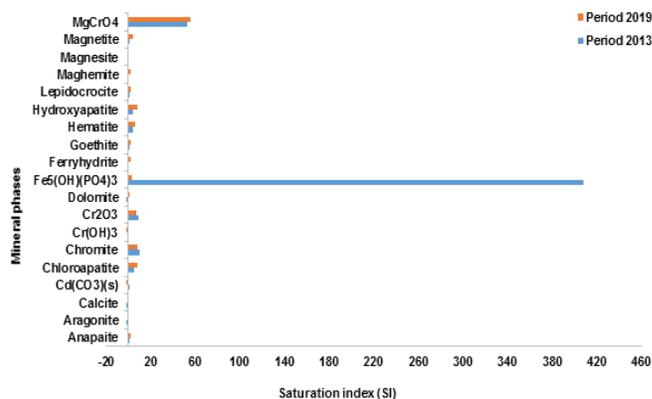


Fig. 2. Saturation index of mineral phases in Namaqualand for 2013 and 2019 period.

The model output showed phases that are governing the groundwater chemistry in the region, with some geochemical reactions being shown to be responsible for the evolution of the groundwater chemistry whereby the dissolution of the carbonate minerals such as aragonite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, calcite dolomite, ferrihydrite and vaterite were identified as initially undersaturated (2013) to supersaturated (2019) with an undersaturation of Cd(CO<sub>3</sub>), Cr(OH)<sub>3</sub> being observed during the same period. Similarly, the precipitation of anapaite, chloroapatite, chromite, Cr<sub>2</sub>O<sub>3</sub>Fe<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub>, ferrihydrite, goethite, hematite, hydroxyapatite, lepidocrocite, maghemite, magnetite was observed, with magnesite evolving from being undersaturated to an equilibrium phase. Gypsum, siderite and halite remained undersaturated, indicating that these minerals may be subjected to continuous dissolution as the groundwater hydrogeochemical evolution is mainly controlled by carbonate mineral dissolutions, cation exchange, precipitation and weathering.

### IV. CONCLUSION

In this research, the integration of hydrogeochemical characteristics techniques and geochemical modelling were used to identify the significant factors governing groundwater hydrogeochemical evolution in Namaqualand. The pH values of the groundwater were alkaline in nature during 2013 and 2019 period. Most of the parameters including EC, TDS, Na and Cl exceeded permissible limits of drinking water standards stipulated by the SANS241-1 [9] and WHO [10]; standards for drinking water. Ca–Mg–HCO<sub>3</sub>, Na–K–HCO<sub>3</sub>, Na–K–Cl–SO<sub>4</sub>, and Ca–Mg–Cl–SO<sub>4</sub> types for both periods (2013 and 2019). The geochemical model PHREEQC suggests some geochemical reactions and mineral phases being responsible for the evolution of the groundwater chemistry and indicating that the groundwater hydrogeochemical evolution is mainly controlled by carbonate mineral dissolutions, cation exchange, precipitation and weathering. The increase in sulfate concentration in period 2019 in groundwater was most likely due to sulfide-mineral oxidation. The contributions of anthropogenic sources were associated with the closed

metalliferous waste, metalliferous waste and acid rock drainage, it is predicted that the risk of PTEs contamination in the study area will probably contribute to groundwater quality degradation. The accumulation of SO<sub>4</sub> in the groundwater maybe due to the arid climate of the area. The typical hypothesis applied at numerous mining locations is that sulfide-mineral oxidation is the main source of sulfate. This information would contribute to risk assessments and evaluation of remediation strategies. It is therefore anticipated that the groundwater contamination will continue to persist in the study area for many years.

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