

ГІДРОГЕОЛОГІЯ, ІНЖЕНЕРНА ТА ЕКОЛОГІЧНА ГЕОЛОГІЯ

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GEOCHEMICAL EVALUATION OF GROUNDWATER QUALITY IN NEWCASTLE, KWAZULU-NATAL, SOUTH AFRICA

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Hydrogeochemical investigations were carried out in Newcastle, in the KwaZulu-Natal province of South Africa to identify the major geochemical processes that control groundwater chemistry. 31 samples were collected and analysed for Magnesium (Mg²⁺), Calcium (Ca²⁺), Sodium (Na⁺), Potassium (K⁺), Chloride (Cl⁻), Sulfate (SO₄²⁻), Bicarbonate (HCO₃⁻), Nitrate (NO₃⁻), Fluoride (F⁻), pH, TDS and EC. Classical hydro-chemical methods; facies analysis and major ion analysis were used to further understand the composition controlling processes. It was inferred from the hydro-chemical facies, major ion scatter plots that the major process affecting the groundwater chemistry in the area is rock-water interaction. The ionic concentration is due to silicate weathering, carbonate weathering and ion exchange processes.

Keywords: Groundwater Geochemistry, Major Ion Chemistry, Hydro-chemical Facies (Water types).

Introduction. The chemistry of groundwater is directly related to the quality of the water and therefore central in determining its use for domestic, irrigation and industrial purposes (Subramani, 2010) [17]. The principal dissolved components of groundwater are six major ions Na⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻ and they constitute 90% of the total dissolved solids (TDS) content. The minor ions include K⁺, Fe⁻, NO₃⁻ and F⁻. Due to human activities such as mining and irrigation, some of these minor ions are raised to higher levels reaching concentrations equivalent to that of major ions (Hiscock, 2005, 2009) [9]. Groundwater composition is mostly influenced by the rocks and other material it traverses through from recharge to discharge. When it flows through geological

formation a number of processes occur which cause an exchange of soluble solids between the rocks and water. Thus mineral composition of the rocks consequently plays a major role in the chemical constituents of groundwater (Elango and Kannan, 2007) [5]. Changes in the concentrations of ions in the water of an aquifer, whether from natural or anthropogenic activities, may alter the suitability of the aquifer system as a source of water (Herring et al., 2002) [8]. Thus, understanding the major processes that control the composition of groundwater is important in effective management of this resource. The study was conducted in Newcastle, in the KwaZulu-Natal province of South Africa (Fig. 1).

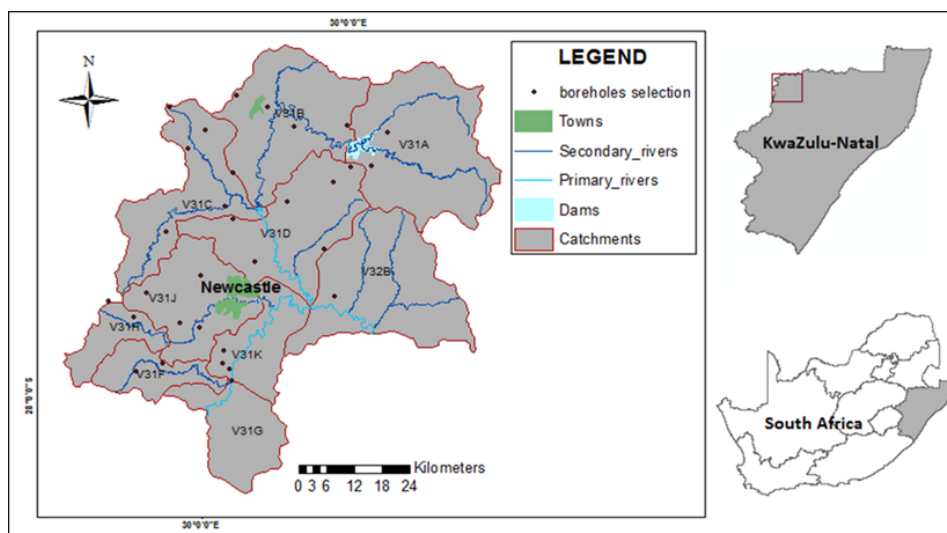


Fig. 1. Study area and location of boreholes

For the purpose of this study 31 samples were collected from 31 boreholes in and around the town of Newcastle. The samples were analysed for Magnesium (Mg²⁺), Calcium (Ca²⁺), Sodium (Na⁺), Potassium (K⁺), Chloride (Cl⁻), Sulfate (SO₄²⁻), Bicarbonate (HCO₃⁻), Nitrate (NO₃⁻), Fluoride (F⁻), pH, TDS and EC.

Geology of Study area. The geology in Newcastle mainly consists of rocks from the Karoo Super Group. Deposition of these sediments began late Carboniferous and continued to accumulate until Early Jurassic when it

was interrupted and eventually brought to a close by widespread flood basaltic volcanism (Catuneanu, 2005) [1]. The rocks that outcrop in the study area belong to Beaufort Group (consisting of mud and sandstone), Karoo Dolerite and the Volksrust Formation (silty shale and sandstone) and Vryheid Formation (consist primarily of sandstone and several coal seams) of the Ecca Group (fig. 2). Of these, however, the Vryheid formation is the most dominant in the study area.

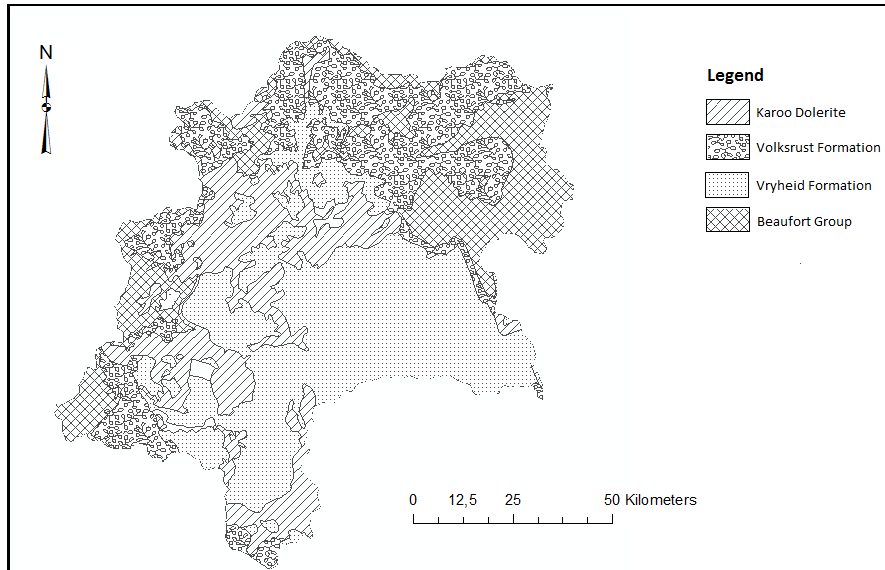


Fig. 2. Local geology of the study area

The indicated aquifer types in the Newcastle area are intergranular and fractured aquifers with an extremely low to medium development potential. The underlying geology is mostly arenaceous rock of the Ecca Formation (DWAf, 2008) [4]. The host geology of the area consists of consolidated sediments of the Karoo Super Group and consists mainly of sandstone, shale and coal beds of the Vryheid Formation. Most of the groundwater flow will be along the fracture zones that occur in relatively competent host rock.

Data Acquisition. The data was supplied by the Department of Water Affairs (DWA). For the purposes of this study 31 samples were used, which were collected from 31 different wells. The wells are located in 10 Quaternary catchments in Newcastle. The samples were analyzed for the following: Magnesium (Mg²⁺), Calcium (Ca²⁺), Sodium

(Na⁺), Potassium (K⁺), Chloride (Cl⁻), Sulfate (SO₄²⁻), Bicarbonate (HCO₃⁻), Nitrate (NO₃⁻), Fluoride (F⁻), pH, TDS and EC.

Results. Hydrochemical Facies. The term hydrochemical facies or water type refers to zones in groundwater that have a distinct level of cations and ions (Hiscock, 2005) [9]. The nature and distribution of hydro-chemical facies can provide insights into how groundwater quality changes within and between aquifers (Sivasubramanian et al., 2013) [14]. These different facies are mainly due to the different kinds of rock-water interaction during groundwater subsurface flow. This classification with the samples from the study area in Piper diagram (Piper 1944) [13], produced four hydro-chemical facies (fig. 3), which are Ca-Mg-HCO₃, Na-HCO₃, Ca-Na-SO₄-HCO₃ (Mixed water type) and Na-Cl.

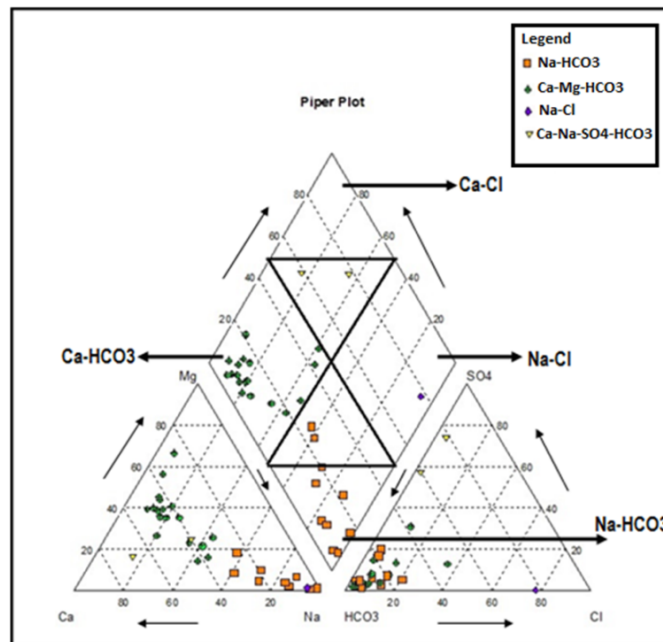


Fig. 3. Piper plot showing hydro-chemical facies in the study area

Map in fig. 4 shows the distribution of the hydro-chemical facies in the study area and their borehole location. The Ca-Mg-HCO₃ facies mainly found in 18 of the

boreholes in the study area, these boreholes are mainly distributed in the Vryheid Fm and in the contact zones between the Karoo dolerite with the Volksrust Fm and with

the Vryheid Fm. This type of water is characterised by combined concentrations of Ca^{2+} , Mg^{2+} and HCO_3^- that exceeds 50% of the total dissolved constituent load in

meq/L. Such waters are typical of fresh and shallow groundwaters. This water type is mainly attributed to the dissolution of carbonate minerals.

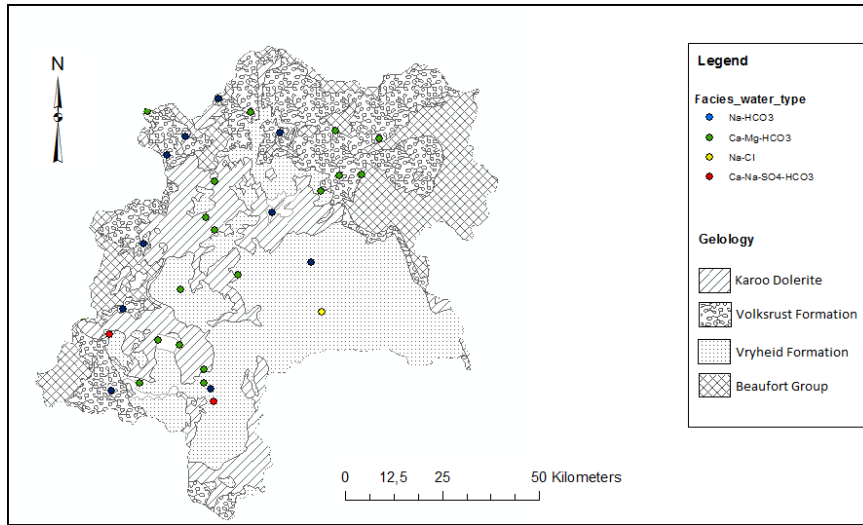


Fig. 4. Map showing spatial distribution of Hydro-chemical facies/water type in the study area

Na-HCO_3 characterises 10 boreholes in the study area, which are situated in the Vryheid Fm and Karoo dolerite. This type of facies generally indicates the occurrence of ion exchange processes in the area. It could also be attributed to silicate weathering, because of the high levels of Na^+ and HCO_3^- which are end products of Albite weathering.

$\text{Ca-Na-SO}_4\text{-HCO}_3$ water type is a product of mixing of types characterises only two boreholes. This water type is mainly distributed in the contacts between the Vryheid Fm and Karoo dolerite. High Ca^{2+} , Na^+ , SO_4^{2-} and HCO_3^- ions in this water type could be attributed to the combined influence of silicate weathering, calcite dissolution, ion exchange processes and gypsum dissolution.

Na-Cl facies is only found in one sample, which is situated in the Vryheid Fm. This facies is characterised by high levels of Na^+ and Cl^- ions, which could be attributed to halite dissolution and ion exchange processes.

Major Ion chemistry. During movement of groundwater through its flow path, a number of processes occur which

gives rise to the ionic composition of the groundwater. The major ion chemistry of the groundwater is the result of these processes and can therefore be used to determine the major processes that are responsible for the composition of the groundwater.

Rock Water Interaction. The TDS vs. $\text{Na}^+ / (\text{Na}^{++}\text{Ca}^{2+})$ and TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ (Gibbs, 1970) [7] scatter plot can be used to identify the occurrence of rock-water interaction processes. The diagram is divided into three fields, the rock-water interaction, precipitation and evaporation. In these diagrams the samples falling in the centre of the curve indicate an origin from rock-water interaction. Fig. 5.a and b represent Gibbs TDS vs. $\text{Na}^+ / (\text{Na}^{++}\text{Ca}^{2+})$ and TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ scatter plots plotted using groundwater samples from the study area. These results show that most of the groundwater samples fall in the centre of the curve, which is indicative of the dominance rock-water interaction as the main process in the study area.

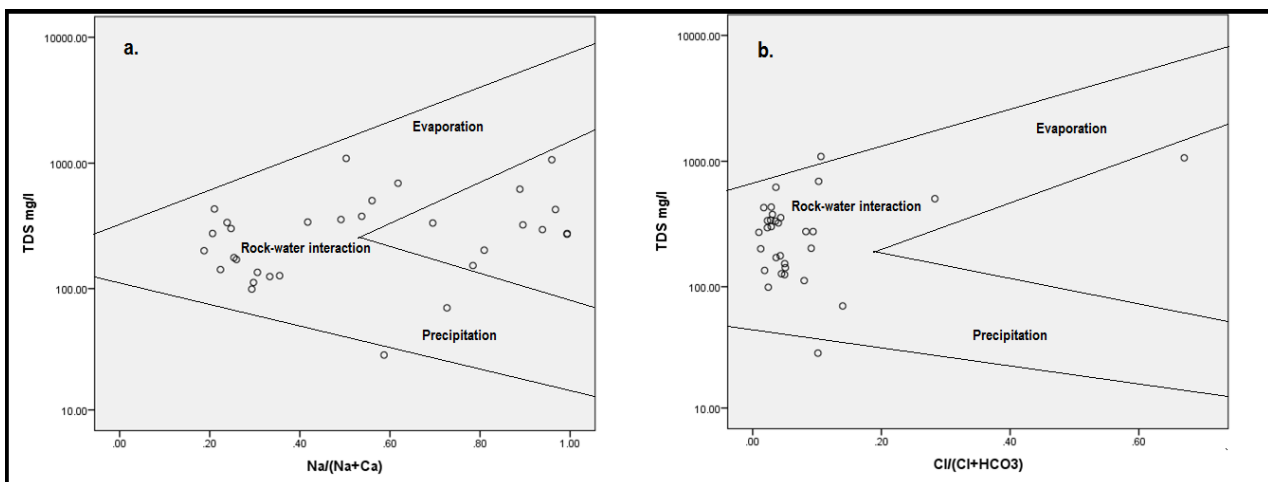


Fig. 5. Rock-water interaction diagram

During the process of rock-water interaction a variety of chemical processes occur such as weathering and dissolution, ion exchange processes oxidation and reduction. The

results in fig. 5.a and b can be further classified into the above mentioned chemical processes by using their concentrations and associations.

Weathering and Dissolution. Carbonate weathering, silicate weathering, halite, gypsum dissolution and precipitation are common in an aquifer system (Elango and Kannan, 2007) [5]. Datta and Tyagi (1996) [3] explained this using the $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$ scatter plot (Fig. 6). They explained that the points falling along the equiline suggest that these ions have resulted from weathering of carbonates, sulphate minerals (gypsum and anhydrite) and silicate minerals. They further explained that those that lie above the equiline are due to silicate weathering while those below the line are due to carbonate weathering.

Fig. 6 represents the $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$ scatter plot plotted using the groundwater samples from the study area, almost 50% of the sample points plot above the equiline, which indicates the dominance of silicate weathering in the study area. While the remaining points plot along the equiline which suggest the combined influence of weathering of carbonates, sulphate minerals (gypsum and anhydrite) and silicate minerals.

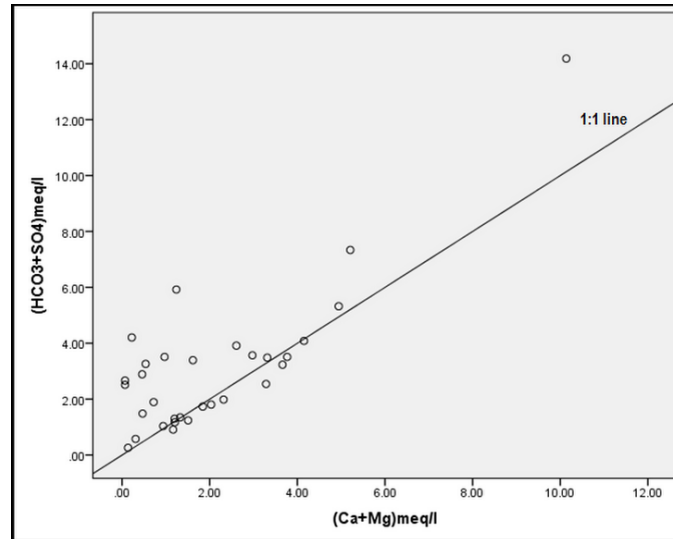


Fig. 6. $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$

In a silicate terrain, if the calcium and bicarbonate in groundwater originated from calcite, the equivalent ratio of dissolved Ca^{2+} and HCO_3^- in the groundwater should be 1:2, whereas if from dolomite weathering, it should be 1:4 (Subramani et al., 2010) [17]. In the Ca^{2+} vs HCO_3^- (fig 7) scatter plot, sample points that plot along the 1:2

line indicate contribution from calcite while those that plot along the 1:4 line indicate contribution from dolomite. Most of sample points from the study area plot along the 1:2 which indicates the dominance of calcite over dolomite as the source.

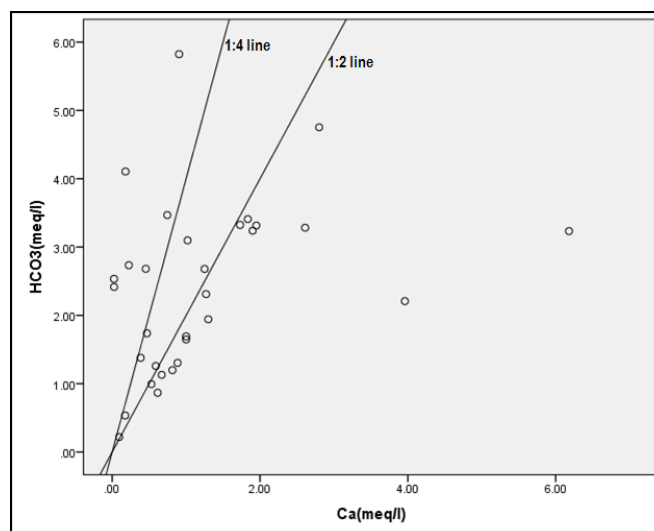


Fig. 7. Ca^{2+} vs. HCO_3^- scatter diagram

Another source of Ca^{2+} and SO_4^{2-} in groundwater systems could be gypsum/anhydrite dissolution. If gypsum/anhydrite dissolution is the major source of the calcium and sulphate in the groundwater then the $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio should be almost 1:1 (Das and Kaur

2001) [2]. Ca^{2+} vs SO_4^{2-} (Fig. 8) shows that most of the sample points plot below the 1:1 line, which indicates the excess of calcium over sulphate and highlights additional geochemical processes as the source of these ions.

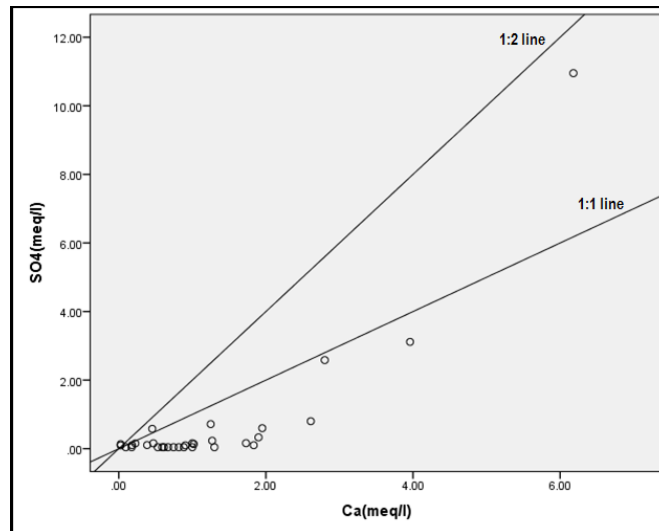


Fig. 8. Ca²⁺ vs. SO₄²⁻ scatter diagram

The contribution of silicate weathering to cation concentration of the groundwater can also be explained (Na⁺ + K⁺)/Total cation index (Stallard and Edmond, 1983; Elango and Kannan, 2007) [5, 16]. The Na⁺ + K⁺ vs. TZ+ (Fig. 9.a) scatter plot shows that majority of the points plot above the 1:1 and near the Na⁺ + K⁺ = 0.5 * TZ+, which sug-

gest that cation in the groundwater might have been derived from silicate weathering. However, there are those few that deviate from this line, this suggest the likelihood of Ca²⁺/Na⁺ exchange processes which might have reduced the amount of Na⁺ in the groundwater.

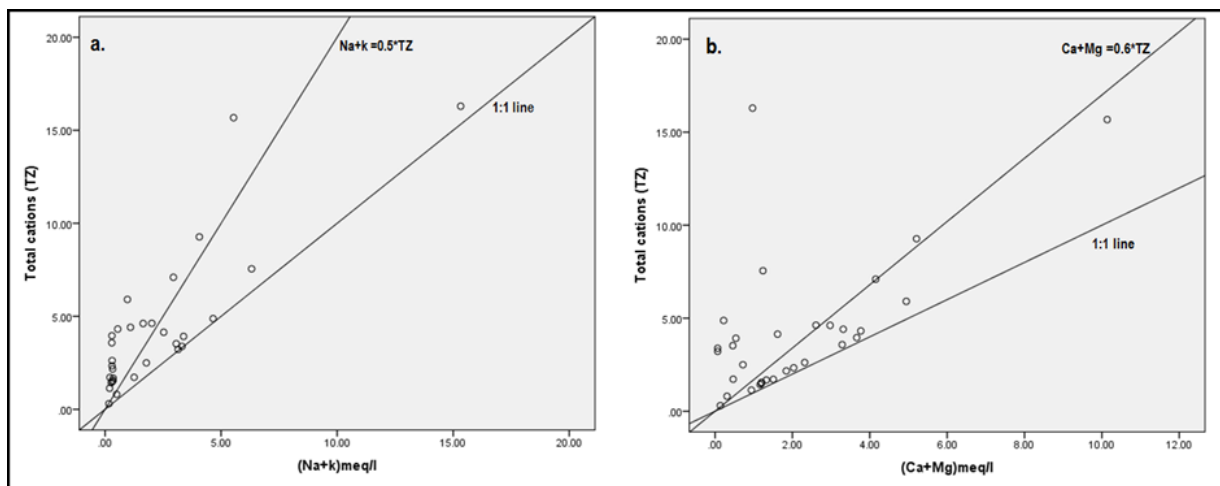


Fig. 9. a: Na⁺+K⁺ vs Total cations (TZ); b: Ca²⁺ +Mg²⁺ vs Total cations (TZ)

The Ca²⁺+Mg²⁺ vs. TZ (fig. 9.b) scatter plot can also be used to verify the role of silicate weathering in cation concentration of groundwater (Maharana et al., 2015) [11]. Majority of the sample points lie above the 1:1 line and along the Ca²⁺+Mg²⁺ = 0.6 * TZ line, this suggest an increasing contribution of Na⁺ and K⁺ from silicate weathering.

The dissolution of halite (NaCl) is understood as one of the major sources of both sodium and chloride in groundwater. In general, when halite dissolution is the source of these ions, Na⁺ vs. Cl⁻ relationship gives 1:1 ratio (Nur et al., 2012) [12]. The Na⁺ vs. Cl⁻ diagram (fig. 10) of the study area shows that most groundwater samples fall below the equiline which indicates that halite dissolution is not the major process responsible for the Na⁺ and Cl⁻ ion concentration in the groundwater. The enrichment of Na⁺ more than Cl⁻ points to silicate weathering as a more likely source of Na⁺ in the water.

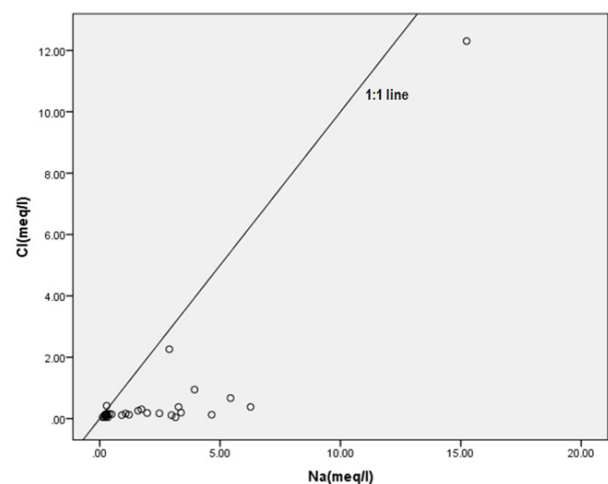


Fig. 10. Relationships between Na⁺ and Cl⁻

Ion Exchange processes. Fisher and Mullican (1997) [6] reported that if ion exchange is a significant composition controlling processes in groundwater, the relationship between $(\text{Na}^+ - \text{Cl}^-)$ vs $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ should be linear with a slope of -1.0 . Fig. 11 shows the

ion exchange scatter plot for the groundwater samples from the study area. The groundwater samples of the study area define a straight line ($R^2 = 0.98$) with a slope of -0.9 , which indicates the occurrence of ion exchange in the study area.

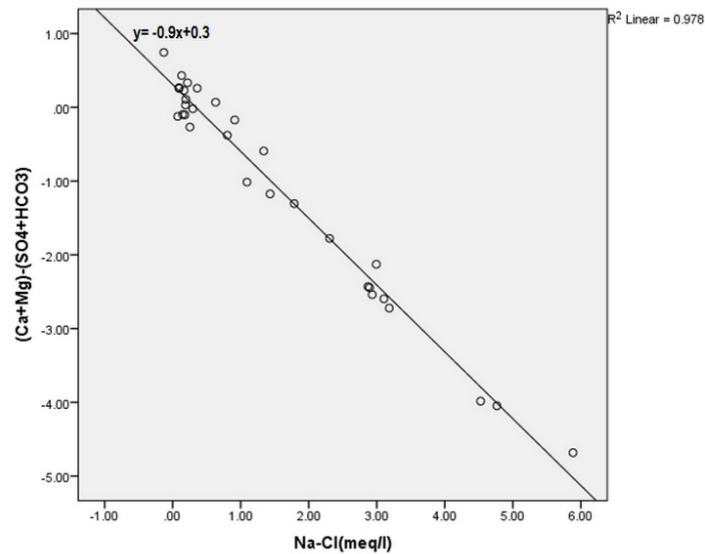


Fig. 11. Ion exchange scatter diagram

Further, it is reported that the plot for $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{SO}_4^{2-} + \text{HCO}_3^-$ can be used as an identifier of ion exchange process (Srinivasamoorthy et. al., 2012) [15]. If normal ion exchange is the process, the points shift to left side of the plot due to excess $\text{SO}_4^{2-} + \text{HCO}_3^-$. If reverse ions exchange is the process, points shift right due to excess $\text{Ca}^{2+} + \text{Mg}^{2+}$. In the $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{SO}_4^{2-} + \text{HCO}_3^-$ (fig. 6) the most points shift to left side of the plot due to excess $\text{SO}_4^{2-} + \text{HCO}_3^-$, which is indicative of normal ion exchange in the study area.

the most of the samples fall toward the $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentration, indicating the occurrence of reverse ion exchange in the area.

$\text{Ca}^{2+} + \text{Mg}^{2+}$ versus Na^+ plot can also be used to indicate the type of ion exchange occurring in an area. A high concentration of $\text{Ca}^{2+} + \text{Mg}^{2+}$ over Na^+ generally indicates reverse ion exchange, while high Na^+ over $\text{Ca}^{2+} + \text{Mg}^{2+}$ indicates normal ion exchange in this plot. Fig. 12 shows

Evaporation. Evaporation is also one of the important processes that affect groundwater chemistry and the Gibbs plot in figure 6 shows some influence of evaporation in some samples in the study area. Na^+/Cl^- ratio could be used to identify the evaporation process in groundwater (Subramani et. al, 2010) [17]. Evaporation will increase the concentration of total dissolved solids in groundwater, and the Na^+/Cl^- ratio remains the same, and it is one of the good indicating factors of evaporation. If evaporation is the dominant process, Na^+/Cl^- ratio should be constant when EC rises (Jankowski and Acworth 1997) [10].

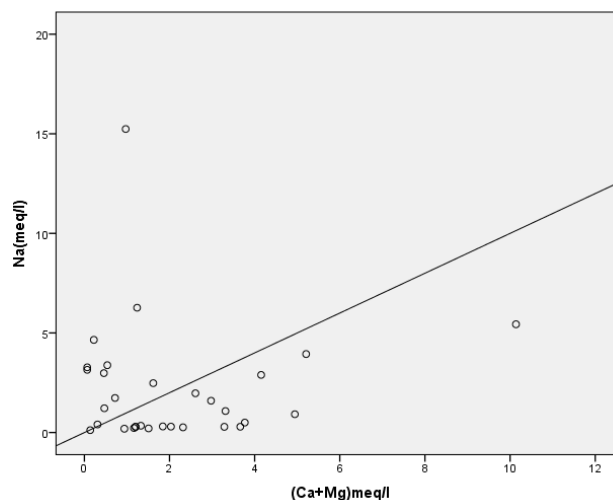


Fig. 12. Na^+ vs. $\text{Ca}^{2+} + \text{Mg}^{2+}$ plot showing increased concentration of Ca^{2+} compared to Na^+ indicating reverse ion exchange

Fig. 13 shows an inclined trend; Na^+/Cl^- ratio slightly decreases with an increase in EC and only a few samples

show an increase the concentration of total dissolved solids in groundwater as Na^+/Cl^- ratio remains constant.

This confirms that evaporation though might have played a part in the concentration of ions in the groundwater in

the study area; it is not the main processes and this is also confirmed by fig. 6.

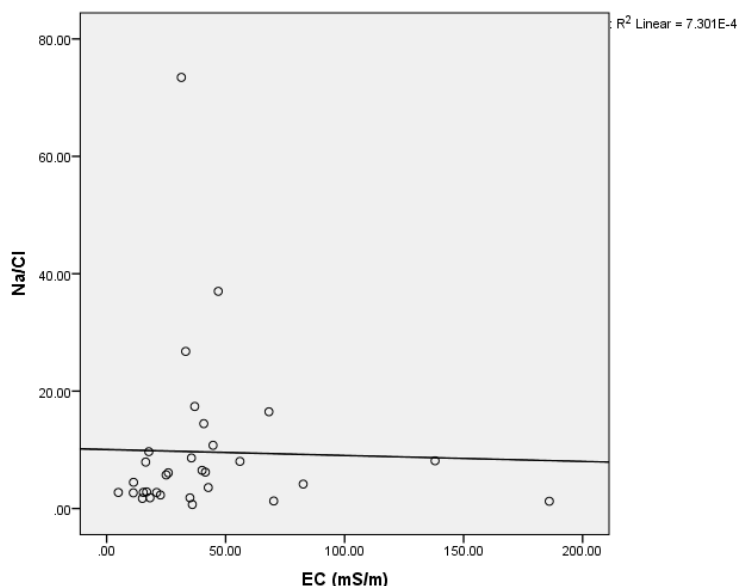


Fig. 13. Relationships between Na+/Cl- and EC

Land use. Apart from the natural/geological controls on groundwater chemistry, land use plays a major role in altering the chemistry of groundwater. The correlation between sulphate and chloride can provide evidence or indicate the effects of surface contamination, especially irrigation return flows. If the correlation is strong it is indicative of a possible

strong influence of land use on groundwater chemistry (Subramani et al., 2010) [17]. Fig. 14 represents the Cl- vs SO4²⁻ scatter plot for the study area. It shows that the relationship between Cl⁻ and SO4²⁻ is not strong, which indicates that land use is not a major composition controlling processes in the study area.

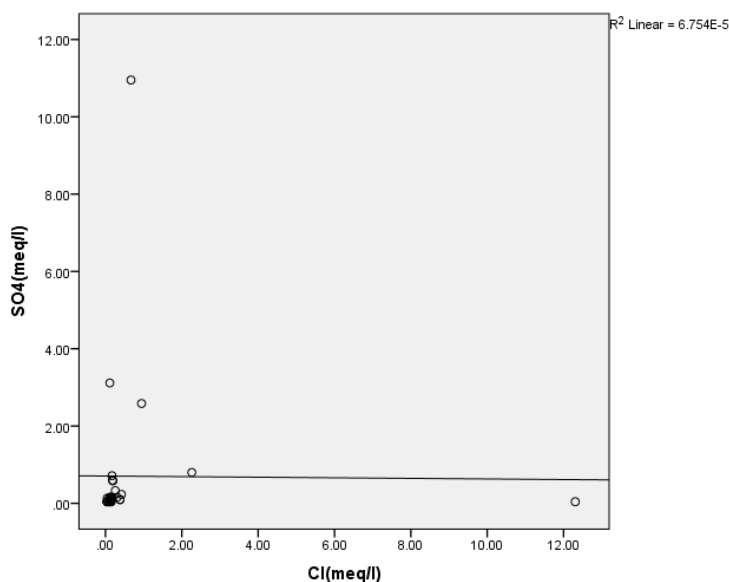


Fig. 14. Cl- Vs SO4²⁻ (effect of land use on groundwater chemistry)

Conclusion. Results of the hydrochemistry suggest that all the water samples are alkaline in nature. Classical hydrochemical methods showed the existence of four hydrochemical facies/water types in the area, the Ca-(Mg)-HCO₃, Na-HCO₃, Mixed water Ca-Na-SO₄-HCO₃ and the Na-Cl water type. The facies show the evolution of groundwater from Ca-Mg-HCO₃ to Na-HCO₃ through silicate weathering and reverse ion exchange processes and to Na-Cl through halite dissolution and ion exchange processes. The Ca-Na-SO₄-HCO₃ water type is a result of mixing of different water

type. The analysis of the major ion chemistry and their spatial distribution indicated the dominance of rock-water interaction as the main process controlling groundwater chemistry in the area. It also indicated the influence of anthropogenic activities in the area. It further showed that the ionic concentration is due to silicate weathering, carbonate weathering, cation exchange (both reverse and normal), gypsum dissolution and halite dissolution, with silicate weathering being the most dominant.

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ГЕОХІМІЧНА ОЦІНКА ЯКОСТІ ПІДЗЕМНИХ ВОД У НЬЮКАСЛІ, КВАЗУЛУ-НАТАЛЬ, ПІВДЕННА АФРИКА

Гідрохімічні дослідження, виконані в м. Ньюкасл у ПАР, у провінції Квазулу-Наталь, дозволили визначити основні геохімічні процеси, що визначають хімічний склад підземних вод. Було відібрано 31 зразок і проаналізовано їх на вміст іонів магнію (Mg^{2+}), кальцію (Ca^{2+}), натрію (Na^{+}), калію (K^{+}), хлору (Cl^{-}), сульфур (SO_4^{2-}), бікарбонату (HCO_3^{-}), нітрату (NO_3^{-}), фтору (F^{-}), визначено рН, загальну мінералізацію води (TDS) та електропровідність (EC). Для більш детального розуміння процесів, що визначають склад води, було також застосовано класичні гідрохімічні методи, гідрофациальний аналіз і аналіз розподілу основних іонів. На основі гідрохімічних фацій, з використанням діаграм розсіювання основних іонів, було зроблено висновок, що головні процеси, які впливають на хімічний склад підземних вод досліджуваної території, це процеси, пов'язані із взаємозв'язками порода-вода. Концентрацію іонів визначають вивітрювання силікатних і карбонатних порід, а також іонообмінні процеси.

Ключові слова: геохімія підземних вод, хімія іонів, гідрохімічні фації (типи вод).

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ГЕОХИМИЧЕСКАЯ ОЦЕНКА КАЧЕСТВА ПОДЗЕМНЫХ ВОД В НЬЮКАСЛЕ, КВАЗУЛУ-НАТАЛЬ, ЮЖНАЯ АФРИКА

Гидрохимические исследования, выполненные в г. Ньюкасл в ЮАР, в провинции Квазулу-Наталь, позволили определить основные геохимические процессы определяющие химический состав подземных вод. Был отобран 31 образец и проанализирован их состав на содержание ионов магния (Mg^{2+}), кальция (Ca^{2+}), натрия (Na^{+}), калия (K^{+}), хлора (Cl^{-}), серы (SO_4^{2-}), бикарбоната (HCO_3^{-}), нитрата (NO_3^{-}), фтора (F^{-}), определены рН, общая минерализация воды (TDS) и электропроводность (EC). Для более полного понимания процессов, определяющих состав воды, также применялись классические гидрохимические методы, гидрофациальный анализ и анализ распределения основных ионов. На основе гидрохимических фаций, с применением диаграмм рассеяния основных ионов, был сделан вывод о том, что основные процессы, влияющие на химический состав подземных вод территории исследования, это процессы, зависящие от взаимных связей порода-вода. Концентрация ионов определяется выветриванием силикатных и карбонатных пород, а также ионообменными процессами.

Ключевые слова: геохимия подземных вод, химия ионов, гидрохимические фации (типы вод).