Hydrochemical Processes Governing Groundwater Chemistry in Al-Wajh Province, Kingdom of Saudi Arabia

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ABSTRACT

Groundwater is a valuable water resource in Saudi Arabia due to the scarcity of sustainable/renewable water sources. Therefore, the systematic and continuous monitoring of groundwater is essential to ensure its effective and sustainable management. This aligns closely with the objectives of the Kingdom's National Water Strategy, which emphasizes the preservation, efficient utilization, and long-term sustainability of groundwater resources to support national development and water security. This study represents a hydrochemical assessment for groundwater sources in ten sites within Al-Wajh municipality, western region of Saudi Arabia. The results indicate that the concentrations of all dissolved ions in the analysed samples exceeded the permissible limits set by the World Health Organisation (2011). Apparently, this groundwater is extremely mineralized and is not appropriate for drinking use without proper treatment. The relative abundance of main ions follows the order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+ > Cl^- > SO_4^{2-} > HCO_3^- > NO_3^-$. This delivery confirms that the strong acidic ions such as sulfate (SO_4^{2-}) and chloride (Cl^-) are predominate over weak acid anions like bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Piper diagram shows that groundwater form mixed facies of CaMgCl, CaCl, and NaCl. The correlation between total dissolved solids (TDS) and the ratios of $Cl^-/(Cl^-+HCO_3^-)$ or $Na^+/(Na^+ + Ca^{2+})$ confirms that evaporation and fractional crystallisation are the key variables influencing chemistry of the groundwater in the investigated area. The results of this investigation provide a preliminary evidence that Na^+, Ca^{2+}, and Mg^{2+} participate in the reverse ion exchange mechanism. Sodium adsorption ratio (SAR) and electrical conductivity (EC) calculations indicate that about 60% of the groundwater samples are inadequate for irrigation purposes. Meanwhile, the Wilcox diagram reveals that 10% of samples classified as disputable, while 90% have high EC values, which render them inappropriate for the irrigation of many crops.

Keywords: Al-Wajh; Saudi Arabia; Groundwater quality; Hydrochemical classification.

1. Introduction

The Kingdom of Saudi Arabia faces significant water scarcity due to its location in an extremely arid region. Its harsh climate, characterized by high temperatures, irregular precipitation, and high evaporation rates, exacerbates the limited availability of water resources (Alhababy and Al-Rajab, 2015). As a result, groundwater plays a critical role in meeting the country's water needs, predominantly for drinking and agricultural purposes. In many regions of the country, groundwater remains the primary and, in some cases, the sole dependable water source (AlSuhaim et. al. 2019). Due to the intensive exploitation of groundwater resources, the rate of depletion has significantly exceeded the natural recharge capacity. This imbalance has led to a marked decline in groundwater quality, primarily characterized by increased salinity (Sharaf, 2013), which is attributed to the accumulation of hydrochemical constituents (Alfaifi, 2019). The quality of groundwater is governed by complex interactions between water and the surrounding geological environment, including soils, sediments, stream pathways, and rock types, as well as prevailing geochemical processes such as dissociation, redox reactions, precipitation, seepage, and ion exchange (Corteel 2005; Brima and Al Bishri 2017). The hydrochemical processes, particularly weathering, aquifer lithology, and the surface water retention capacity are critical in understanding the chemical composition groundwater chemistry (Al-Shaibani 2020). Morover, groundwater reservoirs are increasingly susceptible to contamination from anthropogenic sources, including agricultural runoff, industrial discharges, and domestic wastewater (DeNicola et al. 2015; Abdullatif and Osman 2019). Therefore, comprehensive evaluation of both groundwater quality and quantity is essential to ensure the sustainable management and long-term viability of aquifer resources.

Although extensive research has been conducted on the geochemical classification and quality assessment of groundwater across various regions of the Kingdom, including, Al Madinah (Bokhari and Khan 1992; Shraim et al., 2013 ; Bamousa et al. 2013), Assir (Mallick et al., 2021), Al Ula (Tuomi et al. 2013; Toumi et al. 2015;), Al Qasim (Al Bassam 2006), Hail (Kahal 2024), Tabuk (Masoud and Kehail, 2024) and Odqus (AlSuhaimi et. al. 2019), the groundwater quality and geochemical characteristics of the Al-Wajh region remain largely unexplored. This gap highlights the importance of groundwater continuous monitoring for sustainable resource management, in alignment with the kingdom Vision 2030 objectives, which prioritize natural resource conservation, environmental sustainability, and economic diversification through strengthened water security. In this context, a comprehensive hydrogeochemical study in the Al-Wajh region is crucial for assessing water quality, determining predominant geochemical processes, and supporting sustainable water resource management techniques. Thus, this study aims to characterize the hydrochemical properties of groundwater samples from various locations within Al-Wajh and evaluate their suitability for drinking and irrigation. The gathered data will be compared to World Health Organization (WHO 2011) and Saudi Arabian Standard Organisation (SASO 1984) standards.

Area of the study: geology and hydrogeology

Al Wajh is a coastal province located in the northern Hejaz region of Saudi Arabia, within the northwestern part of the Kingdom. Geographically, it lies along the Red Sea coast in Tabuk Province, between latitude 26°13′ N (26.79°) and longitudes 36°18′ to 37.27° E (Figure 1). The province covers an estimated area of 4.30 Km^2 and has a population of approximately 50,000 inhabitants. The area has a continental desert environment characterized by hot summer temperatures ranging from 23.8°C to 34.6°C and frigid winter temperatures ranging from 19.4°C to 26.7°C. According to data from Saudi Arabia's National Centre for Meteorology, the average annual rainfall in Al Wajh between 1985 and 2019 was 34.8 mm.

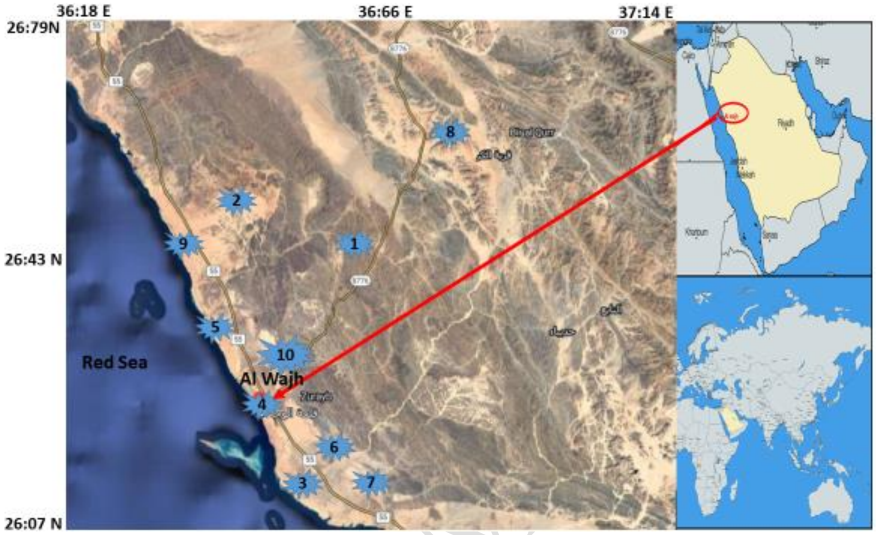

Figure 1. Location map of the study site, Al-Wajh, West of Saudi Arabia

From a geological context, Al Wajh is situated within the Arabian Shield, which consists of many types of basement complex rocks, including igneous, metamorphic, meta-volcanic, and meta-sedimentary rocks. The Upper Saq Sandstone Formation spanned the northern and eastern margins of the Arabian Shield during the early Ordovician period of the Paleozoic epoch, coinciding with the apex of transgression events. Al Wajh is composed of Ediacaran sedimentary rocks and lesser volcanic materials. It also contains Cryogenian tectonic slices that consist of ophiolites, volcano-sedimentary associations, and plutonic intrusions (Johnson et al. 2011; Baggazi et al. 2019). The Saq and its surrounding aquifers, located primarily in the northwest of Saudi Arabia, serve as important water supplies, mainly for domestic and agricultural use. The vast majority of groundwater trapped within Paleozoic and Mesozoic sedimentary formations exhibits a significant level of salt, which has been acquired by prolonged interaction between the water and adjacent rocks (Ahmed et al. 2015).

2. Materials and methods

*2.1. **Sampling and analytical methods***

Groundwater samples were collected from operational borehole wells with depths ranging from 80 to 150 meters during the winter season (January 2018). The samples were stored in 1-liter polyethylene bottles that had been thoroughly precleaned with detergent and deionized water in the laboratory. The bottles were rinsed with samples prior to being filled with sampled water in field. The samples were maintained in an ice box and subsequently transferred to the laboratory, where they were stored in a refrigerator at 4 °C until the analysis. All instruments were calibrated before analysis, following the guidelines of manufacturers. A digital Jenway 3510 pH and Jenway 4510 conductivity mete (Cole-Parmer, Vernon Hills, Il, USA) used to measure pH and conductivity. The conductivity meter standardized with anhydrous KCl solution (0.01N) set at 25 ^{o}C. The preparation and analysis of groundwater samples were carried out at the Faculty of Science and Arts in Al Ula, following the standardized procedures established by the American Public Health Association (APHA, 1998) and as documented in previous studies (Muhammad et al., 2021; Muhammad et al., 2024). The total dissolved solids (TDS) concentration is determined using the residual on evaporation method, which involves evaporating a known volume of water and measuring the mass of the remaining solid residue. Cl^- was determined via titration that used a standard $AgNO_3$ solution and K_2CrO_4 (5% solution) as indicator. The concentrations of Ca^{2+} and Mg^{2+} ions were quantified using a standardized ethylenediaminetetraacetic acid (EDTA) solution and used to calculate total hardness and the bicarbonate (HCO_3^-) ion was titrated with HCl. Flame photometry (Shimadzu, Tokyo, Japan) was utilized to quantify Na^+ and K^+ ions. Colorimetric determination of SO_4^{2-} and NO_3^- was performed utilizing a DR/ 800 Colorimeter (HACH Company, 1997-2004, USA)). The DR/ 800 Colorimeter procedure guide contains a detailed description of how to measure each of these parameters. The accuracy of the analytical procedure was evaluated using the matrix spiking method. The samples had been examined both prior and after each analyte was added in measured quantities and quantified.

Measurements have been performed in triplicate in order to ensure repeatability and quality control. The standard deviations for the mean recovery (accuracy) and the percent recovery (precision) were 2.1 and 98.6, respectively. Equation (1) was used to calculate the precision of quantitative determination of the analysed ions as well as the absolute error in ionic balance.

$$\%\, difference = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \, x\, 100 \qquad (1)$$

In this equation, total cation concentrations in meq/l must match total anion concentrations accurately. The statistical analyses in the study have been carried out using the Statistical Package for Social Science (SPSS) software and Origin 8.5.

3. Results and Discussion

*3.1. **Hydrochemistry and groundwater types***

*3.1.1. **General physical and chemical parameters***

Table 1 presents the statistical data of the analyzed parameters, including lowest, highest, average, and standard deviation, for the investigated chemical constituents in analyzed groundwater samples. The pH readings for the water samples fall between 6.95 and 8.9, with a mean value of 7.8, indicating the basic nature of samples. The pH levels were found to be within the permitted range of 7 to 8.5 as per the WHO 2011 criteria. TDS levels in the water samples were ranged from 1,283 to 12,152 mg/L on average, reflecting a clear mineral dissolution (Choi et al. 2005).

As stated by Davis and De Wiest(1966), groundwater is often classified based on its TDS content. They consider groundwater that contains a TDS value of 500 mg/L or lower to be acceptable for drinking, groundwater with a TDS value between 500 mg/L and 1,000 mg/L to be appropriate for drinking, and that has a TDS value of about 3,000 mg/L or higher to be unsafe for drinking (inadequate for consumption). The electrical conductivity (EC) at 25°C varies between 2,600 and 23,660 µS/cm, with an average of 11,215 µS/cm, suggesting a high concentration of soluble salts in the groundwater of Al-Wajh. All samples surpass the maximum permissible limit of 1,500 µS/cm set by the EC. The elevated salinization values are mostly attributed to the ion exchanges and solubilization processes occurring inside aquifers (Sanchez-Perez and Tremolieres 2003). All groundwater samples in the studied area are unsuitable for human consumption.

Table 1: Results of the chemical composition of different constituents in the groundwater samples

Parameters	Units	Minimum	Maximum	Mean	SD
pH	-	6.95	8.9	7.8	0.68573
EC	µS/cm	2,600	23,660	11,215	7,223.51
TDS	mg/L	1,283	12,150	5,629.3	3,670.77
Ca^{2+}	mg/L	220	2,460	982.5	737.621
Mg^{2+}	mg/L	56	380	168.8	103.707
Na^{+}	mg/L	270	2,511	1,156.6	817.082
K^{+}	mg/L	12	125	52.8	37.8089
NO_3^{-}	mg/L	2	15	7	4.13656
CO_3^{2-}	mg/L	0	35	8	13.3749
Cl^{-}	mg/L	580	5,448	2,214.1	1,460.1
HCO_3^{-}	mg/L	140	1,750	649	526.797
SO_4^{2-}	mg/L	410	3,570	1,357.8	1,235.7
PO_4^{3-}	mg/L	0.162075	3.54	0.8368075	1.01031

3.1.2. Major ion chemistry

The primary cations present in groundwater samples was sodium, with the predominant distribution of ions being Na+ followed by Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, and NO_3^{-}. The calcium level was found to fluctuate between 220 and 2,460 mg/L, with an average value of 982.5 mg/L. Out of the samples analyzed, only one contained calcium at a level considered acceptable, specifically 250 mg/L. On the other hand, 60% of the samples meet the suggested acceptable level of magnesium, which is 200 mg/L, as stated by SASO (1984) and the WHO (2011). The sodium and potassium concentrations fell between the limits of 270–2511 and 12-125 mg/L, respectively. The concentration of Na ions in all samples exceeds the allowable limit of 200 mg/L. The inability of potassium minerals to break down during weathering may be the cause of the shortage of potassium in aquifers (Golditch 1938).

The major ions detected in the tested groundwater samples from the research region were Cl^{-}, followed by SO_4^{2-} and HCO_3^{-}. The chloride concentration ranges from 580 to 5448 mg/L. According to Maiti(1982), elevated level of Cl^{-} in groundwater is a recognized factor in the development of hypertension, osteoporosis, renal stones, and asthma. This investigation revealed a range of bicarbonate (HCO_3^{-}) concentrations in the groundwater samples, spanned from 140 to 1,750 mg/L. according to WHO (2011) standards, the concentration of HCO_3^{-} should not surpass 250 mg/L, despite the lack of any known adverse effects on human health. The average concentration of SO_4^{2-} in this particular area is 1,357.8 mg/L, ranging from 410 to 3,570 mg/L (Table 1). A high level of nitrate (Majumdar and Gupta 2000) can lead to many health complications such as methemoglobinemia, stomach cancer, goitre, anomalies in birth, and hypertension. The examined water samples exhibit NO_3^- concentrations ranging from 2 to 15 mg/L, which fall below the established threshold values of 45 mg/L (SASO 1984; WHO 2011).

3.1.3. The origin of solutes

Figure 2a demonstrates a clear positive correlation (r = 0.99) between TDS (mg/L) and EC (µS /cm), with a slope of 0.51 that aligns closely with the widely acknowledged approximate correlation (Hem 1989). The computed cation-anion balance value appears to be close to the 5% threshold, which coincides with the generally accepted range of hydrogeochemical values. The relationship between total cation (TCC) and anion (TAC) concentration is apparent in Figure 2b. A regression analysis with a coefficient of determination of 0.994 provides strong evidence in support of the stated perspective.

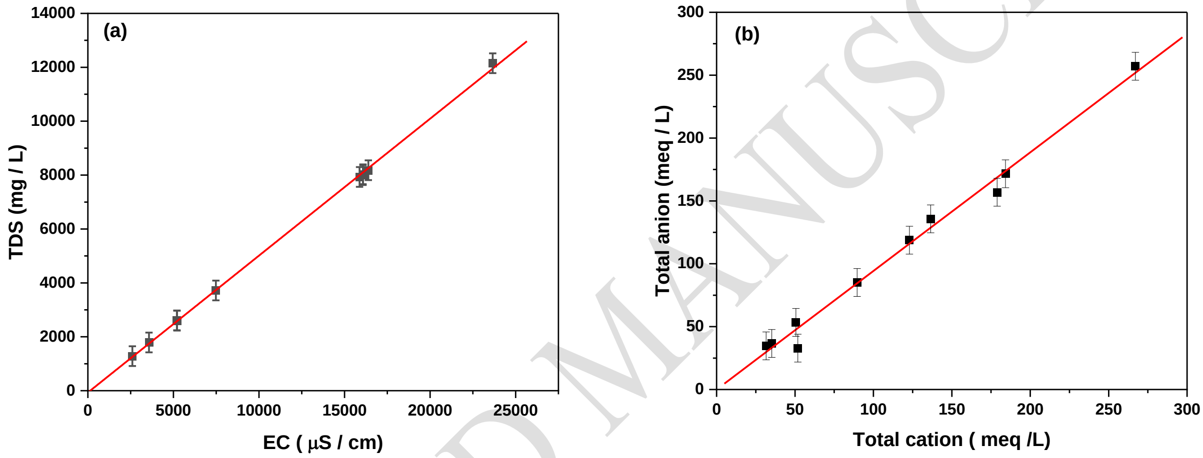

Figure 2. Correlation between TDS and EC (a); Total anion and cation (b)

The binary correlation of soluble salts can reveal the source of solutes and the fundamental hydrochemical processes comprising cation exchange, ion addition or removal, and dissolution. The correlation between anions and cations in meq/L could be examined using gradients, which provide valuable insights into the stoichiometry of the geochemical process (Ghimire, et al. 2023). The presence of strong correlations implies that the pattern is more likely to be attributed to natural process, mainly the lithology of country rocks, rather than anthropogenic activities (Kouser, et al., 1987). Carbonate minerals are the principal source of Ca^{2+} and Mg^{2+} in groundwater. The main source of HCO_3^- is the dissolution of minerals, such as calcite and dolomite. The oxidation of organic substances leads to the release of carbon dioxide (CO_2), which acts as a secondary source of bicarbonate ions (HCO_3^-)(Srinivasamoorthy et al 2011; Zilberbrand et al 2001). The studied region shows a poor association between Ca^{2+} and Mg^{2+} with HCO_3^- (r = 0.59 and 0.56, respectively). Further investigation into the relationship between (Ca^{2+} + Mg^{2+}) and HCO_3^- has shown that the data sets above the 1:1 line, as depicted in Figure 3a, due to the effects of cation exchange mechanisms (Kuma et al 2009). The water samples being examined indicate a higher concentration of Ca^{2+} + Mg^{2+} compared to HCO_3^-. This suggests the existence of additional sources of Ca^{2+} and Mg^{2+}, which are balanced by other anions. The high concentration of Ca^{2+} + Mg^{2+} compared to HCO_3^- may be attributed to severe aridity, carbonate weathering, and revers ion exchange process in favourable lithology (Al-Bassam et al 1997). The ratio of (Ca^{2+} + Mg^{2+})/ HCO_3^- was found to be higher than 0.5. If Ca^{2+} and Mg^{2+} were exclusively generated via carbonate dissolution in aquifer materials, the resulting ratio would be approximately 0.5 (Sami 1992). Reverse ion exchange, in which the aquifer materials absorb Na^+ and release Ca^{2+} and Mg^{2+} ions into water (e.g. the dominance of Ca and Mg ions over Na ions has been explained by reverse ion exchange process), observed in hard rock formations as salinity increases, could potentially contribute to the presence of Ca^{2+} and Mg^{2+} due to the elevated Ca/HCO_3 molar ratios (> 0.5). The ratio of (Ca^{2+} + Mg^{2+})/ HCO_3^- is a useful to gain insights about the sources of Ca^{2+} and Mg^{2+} ions in groundwater. It is believed that dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) are unlikely to be the primary sources of Ca^{2+} and Mg^{2+}, as the presence of bicarbonate (HCO_3^-) in the aquifer indicates that silicate weathering may be the dominant geochemical process influencing the ionic composition (Elango and Kannan, 2007). In addition, significantly higher concentrations of Cl^- and SO_4^{2-} in relation to HCO_3^- imply that silicate weathering played a limited role in the geochemical evolution of groundwater in this area. The binary connection between Ca^{2+} + Mg^{2+} and SO_4^{2-} shows a strong Pearson correlation ($r = 0.87$) and deviates significantly from the 1:1 line (Figure 3b). This indicates that anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$) are not the main sources of Ca^{2+} and Mg^{2+} ions contained in this type of aquifers .The strong link observed between the Ca^{2+} + Mg^{2+} and SO_4^{2-} suggests that these minerals possibly originated from rocks that contain dolomites and gypsum (Figure 3b).

The dissolution of calcite, dolomite, and gypsum is expected to produce Ca^{2+}, Mg^{2+}, and HCO_3^- ions, which lead to a balanced charge between cations and anions (Jalali 2009). The groundwater samples from the investigated area have lower concentrations of (HCO_3^-+ SO_4^{2-}) compared to (Ca^{2+} + Mg^2) (Fig. 3c). If the main processes are the dissolution of calcite, dolomite, anhydrite, and gypsum, the Ca^{2+} + Mg^2/ HCO_3^-+ SO_4^{2-}ratio would be 1(Venugopal et al. 2009). The result shows that Ca^{2+} + Mg^{2+} is prominent over HCO_3^- + $SO_4^{2-,}$ indicating that there is potential for reverse ion exchange.

The correlations of Cl^- vs. Ca^{2+} and Mg^{2+} indicate significant positive correlations ($r = 0.90$ and $r = 0.80$, respectively). The Ca^{2+} + Mg^{2+} versus Cl^- plot shows that the majority of the groundwater samples are clustered near the 1:1 line ($r = 0.89$; **Figure 3d**). These findings confirm that a potential portion of the calcium and magnesium originate from chloride sources. Figure 3e, illustrates a significant positive association between Na^+ and SO_4^{2-} ($r = 0.71$) and about 20% of the experimental results are within a mille-equivalent ratio of 1:1, which imply that the Na^+ in these samples is predominantly might results from the dissolution of Na^+ sulphate minerals.

Computing the ratio of Na^+ and K^+ concentrations to total cation concentrations allows for a better understanding of silicate weathering (TC) mechanisms.

The plot in Figure 3f clearly illustrates that the correlation between $Na^+ + K^+$ and total cations (TC) is near to the $Na^+ + K^+ = 0.44$ TC line. This suggests that silicate weathering is not the main factor in the geochemical processes in the area (Rajmohan and Elango, 2004; Rahman et al 2023).

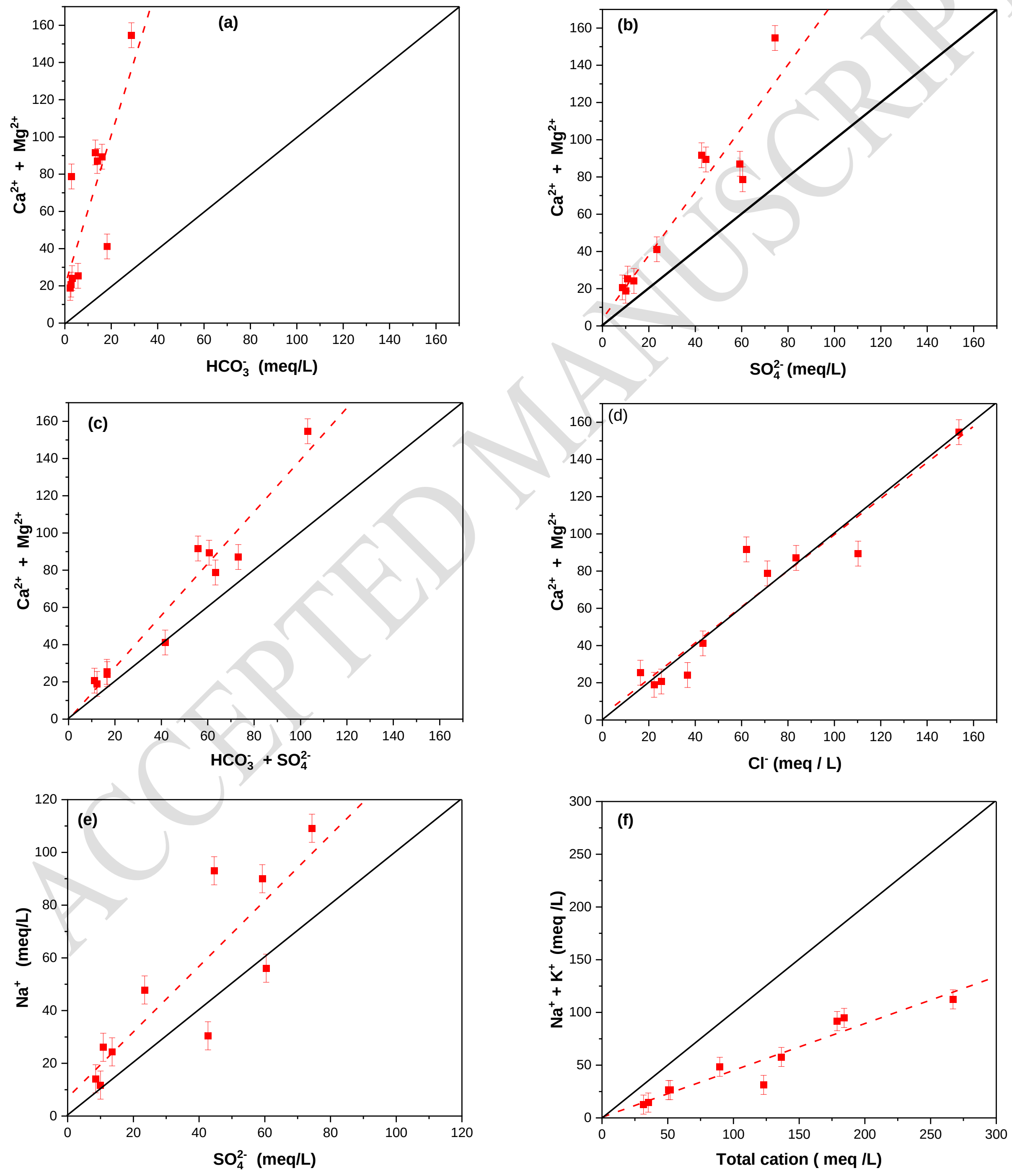

Figure 3. Relationships between ion concentrations for Cl^-, HCO_3^-, SO_4^{2-} , Ca^{2+}, Mg^{2+}, Na^+ and K^+. Solid line denotes 1:1 meq/L.

The relationship between chloride ($Cl^−$) and sodium (Na^+) concentrations in groundwater is a key indicator for evaluating salinity development and the occurrence of saline intrusions in semi-arid regions (Magaritz et al., 1981; Dixon and Chiswell, 1992). A strong positive correlation between Na^+ and $Cl^−$ concentrations is evident in the groundwater samples (r = 0.85), as illustrated in Figure 4a. However, the deviation of this relationship from the expected 1:1 molar ratio, with values falling below the equiline, suggests that halite dissolution is not the primary source of sodium in the studied groundwater. The amount of sodium and chloride generated during the dissolution of halite in water is equivalent. Occasionally, plotted values above the 1:1 equiline reflect atmospheric contributions originating from the Red Sea. The Na/Cl ratio in seawater typically stands at 0.86. According to Meybeck (1987), a molar ratio of Na/Cl greater than 1 indicates the influence of sodium release due to silicate weathering. The mean Na/Cl molar ratio in the studied region is 0.84, with a range of 0.49 to 1.59. This means that a considerable proportion of the alkalis present in the analysed groundwater samples may have originated from the process of silicate mineral weathering and the breakdown of halite.

The ratio of Na^+ to the total Na^+ and Cl^- can be exploited to identify the origin of sodium ion. A $Na^+ / (Na^+ + Cl^-)$ ratio below 0.5 indicates that the water is derived from reversed ion exchange (Hounslow 1995), whereas, $Na^+ / (Na^+ + Cl^-)$ ratio of 0.5 suggests that the water could have come from the dissolution of halite. Figure 4b illustrates that around 70% of the analyzed samples has a $Na^+ / (Na^+ + Cl^-)$ ratio bellow 0.5, indicating that the probable source of the water is the reverse ion exchange process.

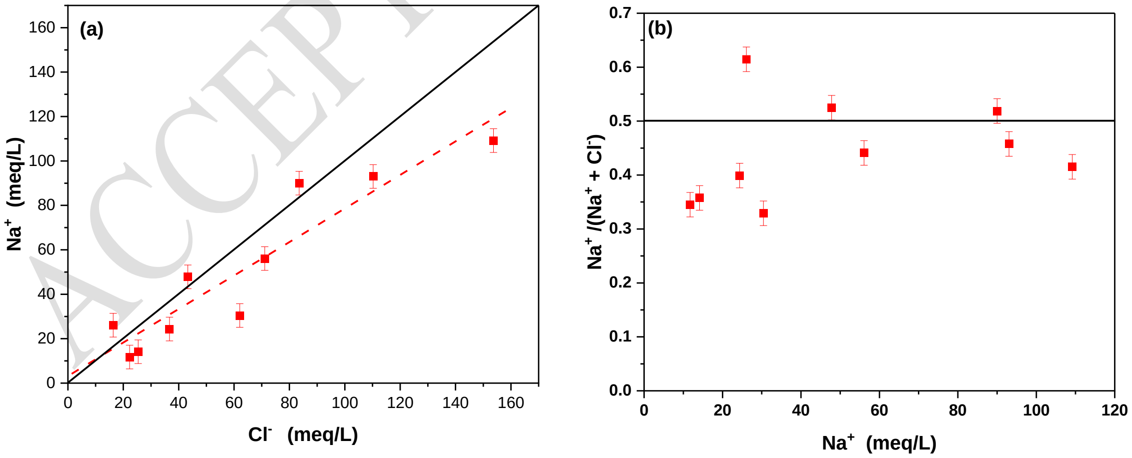

Figure 4. Sodium ions as a function of chloride ions (a), Na/(Na+Cl) as a function of Na in meq/L (b)

The $Ca^{2+} + Mg^{2+}$ versus Na^+ plot (**Figure 5a**) shows that $Ca^{2+} + Mg^{2+}$ dominates the level of Na^+ present in groundwater. This indicates that the reverse ion exchange is a prevailing mechanism

[(Jankowski and Acworth, 1997; Gao et al. 2007). The relationship between (Ca^{2+}+Mg^{2+})-(HCO_3^--SO_4^{2-}) and (Na^+- Cl^+) has already been studied to give more information about the Ca^{2+} and Mg^{2+}, and Na^+ ion exchange (Fisher and Mulican 1997) If Na^+, Ca^{2+}, and Mg^{2+} take part in the ion exchange process, the (Ca^{2+}+Mg^{2+})-(HCO_3^--SO_4^{2-}) and (Na^+- Cl^+) plot will show a slope of 1.0. Na^+, Ca^{2+}, and $Mg^{2+}$are confirmed to be involved mostly in reverse ion exchange process in the majority studied samples (**Figure 5b**) (Garcia et al., 2001; Jalali 2005).

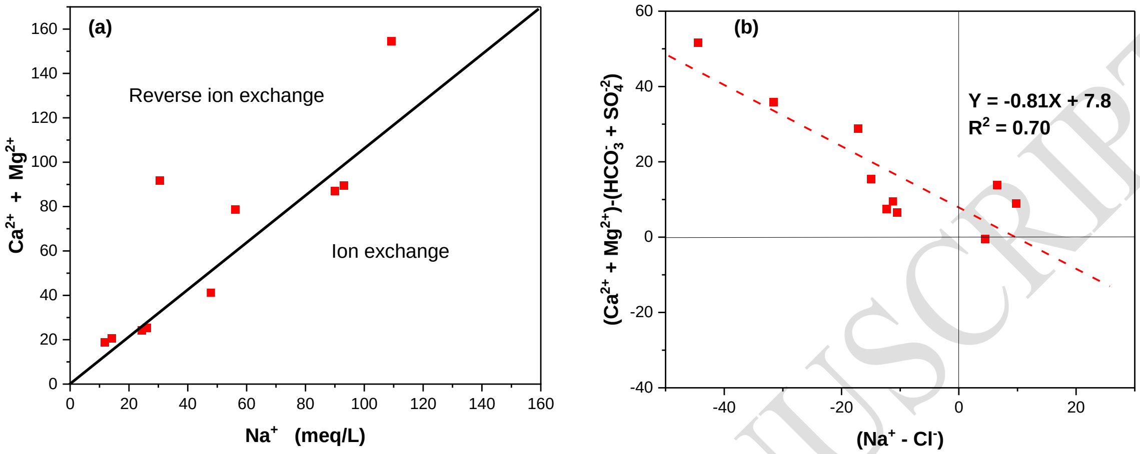

Figure 5. Scatter diagrams showing relationship between a Na^+ vs (Ca^{2+} +Mg^{2+}) (a) and Na^+– Cl^- vs (Ca^{2+}+ Mg^{2+}) - (HCO_3^-+SO_4^{2-}) (b).

3.1.4. Hydrogeochemical classification of groundwater

The nature of groundwater is indicative of the hydrogeochemical characteristics of the aquifer system with which it is associated. Groundwater can be classified into distinct groups based on its chemical composition (Piper, 1944). In semi-arid environments, the development of salinity and the occurrence of saline intrusions are influenced by the interaction between chloride (Cl^-) and sodium (Na^+) concentrations in groundwater (Magaritz et al., 1981; Dixon and Chiswell, 1992). The chemical data presented in the Piper trilinear diagram (**Figure 6**) indicate that the water samples primarily belong to the mixed Ca-Mg-Cl facies, followed by the Ca-Cl and Na-Cl facies. Chloride is the dominant anion, while no single cation exhibits clear dominance (Todd and Mays, 2005). Based on the Piper diagram, the water samples consistently exhibit higher concentrations of strong acids (Cl^- and SO_4^{2-}) compared to weak acids (HCO_3^- and CO_3^{2-}). The comparison between Ca^{2+} + Mg^{2+} and Na^+ reveals that Na^+ dominates over Ca^{2+} + Mg^{2+} in 50 % of the samples.

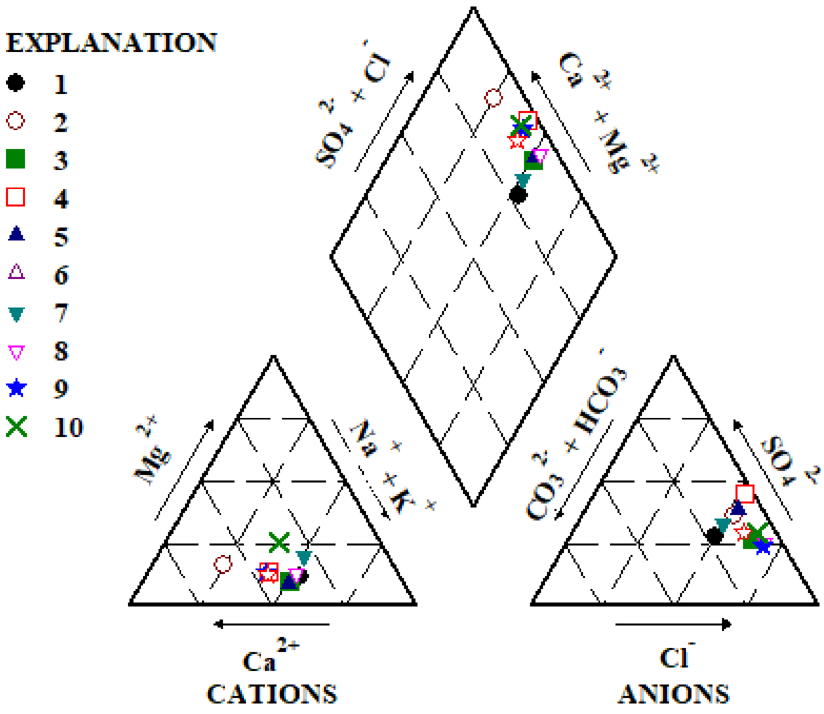

Figure 6. Piper diagram for major ion composition (meq/ L) of groundwater samples

3.1.5. Controlling mechanism (Gibbs 1970)

According to Gibbs (1970), plotting a graph of TDS versus the weight ratio of $Na^+/(Na^+ + Ca^{2+})$ or $Cl^-/(Cl^- + HCO_3^-)$ provides valuable information on the underlying processes that control the chemistry of water. These include the processes of atmospheric precipitation, evaporation, fractional crystallisation, and the weathering of minerals that comprise up rocks (such as carbonates, silicates, and sulphides). $Na^+/(Na^+ + Ca^{2+})$ concentrations in the investigated area vary from 0.29 to 0.63, while TDS concentrations range from 1283 to 12150 mg/L. The Gibbs plot (Figure 7) confirms that the evaporation is a dominance due to the arid climate in the region; with fractional crystallization further elevating salinity through ion concentration. Moreover, the rapid evaporation rate increases Na^+ and Cl^- concentrations sharply, the TDS value raise and hence the salinity level. The evaporation also accelerates the chemical weathering process, which raises the concentration of dissolved ions and hence influences the salinity.

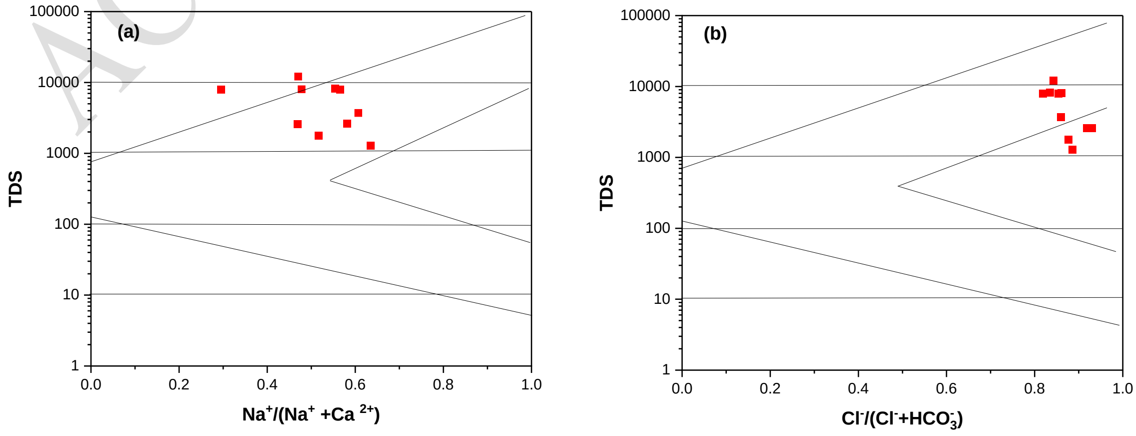

Figure 7. Gibbs plot showing major processes controlling groundwater chemistry

3.1.6. Ion exchange process

Scholler's chloro-alkaline indices (Scholler 1977), CAI-1 and CAI-2, are valuable tools for understanding ion exchange interactions in groundwater and its host environment, either one is residing or travelling. Equations 2 and 3 are utilised to calculate the chloro-alkaline indices that are applied in the evaluation of base-exchange process.

Chloro alkaline index 1 $$\mathrm{CAI}-2=\frac{[\mathrm{Cl}^{-}-(\mathrm{Na}^{+}+\mathrm{K}^{+})]}{(\mathrm{Cl}^{-})} \quad (2)$$

Chloro alkaline index 2 $$\mathrm{CAI}-2=\frac{[\mathrm{Cl}^{-}-(\mathrm{Na}^{+}+\mathrm{K}^{+})]}{(\mathrm{SO}_4^{2-}+\mathrm{NO}_3^{-}+\mathrm{CO}_3^{2-}+\mathrm{HCO}_3^{-})} \quad (3)$$

The base-exchange mechanism, also referred to as the chloro-alkaline equilibrium, is evidenced by an increase in the index value resulting from the exchange of Na^+ and K^+ ions in water with $Mg^{2+}$and Ca^{2+} ions.When Schoeller index has a negative value, there most be an imbalance in chloro-alkaline levels. This phenomenon is known as a cation-anion exchange reaction (Scholler 1977).The chloroalkaline index (CAI) for aquifer samples in this study varied from -.61 to 0.49, with an average value of 0.14. Meanwhile, the CAI-2 index values ranged from -0.61 to 0.78, with an average value of 0.29 (Table 2). Approximately 70% of the samples display positive ratios, indicating a direct base-exchange behavior.

Table 2: Classification of Groundwater samples on the basis of CAI 1, CAI 2 (Scholler 1977), SAR, RSC, Na%, PI (Richards 1954), KR, and CR.

Station number	CAI 1	CAI 2	SAR	RSC (meq/L)	Na %	PI	KR meq/L	CR
1	-0.12	-0.12	10.5	-22.9	54.07	58.55	1.16	4.68
2	0.49	0.55	4.5	-78.5	25.46	27.89	0.33	9.44
3	0.14	0.26	13.9	-73.4	51.45	53.19	1.04	12.08
4	0.19	0.21	8.9	-75.9	42.31	42.85	0.71	40.38
5	-0.09	-0.11	13.6	-73.1	51.32	52.93	1.03	12.85
6	-0.61	-0.61	7.3	-19.8	50.94	55.27	1.02	6.06
7	0.28	0.61	7.0	-21.1	52.21	53.83	1.01	21.05
8	0.43	0.97	4.4	-18.0	41.26	45.26	0.68	16.97
9	0.27	0.39	12.4	-125.	42.08	43.41	0.71	10.22
10	0.43	0.78	3.8	-16.6	40.05	43.24	0.62	18.17

3.2. ***Irrigation water quality***

The presence of inorganic ions in water significantly influences both soil structure and crop development (Zaman et al., 2018). Indicators such as the Sodium Adsorption Ratio (SAR), Permeability Index (PI), Percentage of Sodium (%Na), and Residual Sodium Carbonate (RSC) are commonly employed to assess the suitability of water for irrigation purposes.

*3.2.1***. *Sodium adsorption ratio (SAR) and US salinity diagram (USSL)***

SAR values (calculated using equation (4)) are the most reliable predictor of the adequacy of groundwater for irrigation. Ayers and Westcot (1985) stated that irrigation water can be categorised based on SAR values. Water with SAR values between 0 to 10, which is low in sodium, poses a minimal risk of exchangeable sodium. Water with a moderate salt content, as indicated by SAR values ranging from 10 to 18, may cause a substantial hazard. Water with high sodium content, particularly with SAR values ranging from 18 to 26 and over 26, is considered undesirable due to the potential risk of high exchangeable sodium in soils. The SAR values of all samples within the research zone range from 3.8 to 13.9. This indicates that 60% of the samples belong to the low apparent hazard class.

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)/2}} \qquad (4)$$

Where the ionic concentrations are all reported in meq/L.

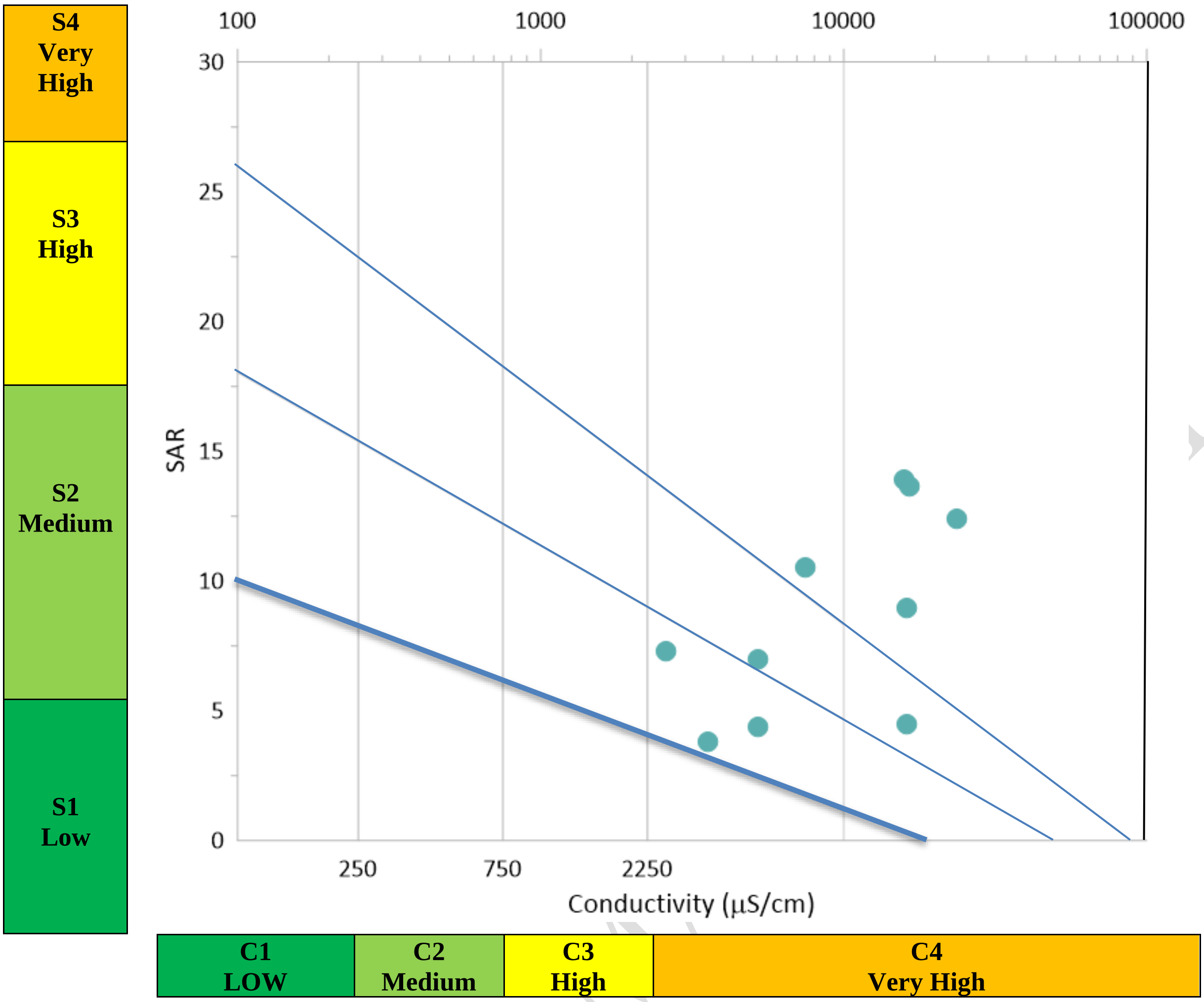

Figure 8. Classification of irrigation waters by USSL (after Richards 1954)

The majority of Alwajh's groundwater has salt levels exceeding 2,250 µS/cm. Consequently, the USSL Staff (1954) water categorization diagram has been adjusted to include higher levels of salinity, specifically expanding the range to 30,000 µS/cm (Shahid and Mahmoudi 2014). The US Salinity Lab diagram has been utilised by plotting SAR and EC values. Figure 8 illustrates that a significant proportion (30.00%) of the groundwater samples in field C4-S2 exhibit high salinity and low sodium levels. This water can be safely used for irrigation on various types of soil without the risk of excessive sodium content. In addition, a small percentage (20%) of samples falling into the C4-S3 group, reflecting high salinity and low alkalinity. While this type of water may not be optimal for drainage purposes, it can still be used for plants that have a high tolerance for salt (Hem 1989). The majority of the sample, almost 50%, falls into the high salinity risk category (C4-S4), rendering them unsuitable for irrigation purposes.

*3.2.2. **Residual sodium carbonate (RSC)***

RSC is commonly used to figure out the possible impact of CO_3^{2-} and HCO_3^- on the agricultural water supply. It is computed using equation (5) (Eaton 1950; Ragunath 1987). The appropriateness of groundwater for irrigation is influenced by the enhanced levels of CO_3^{2-} and HCO_3^- ions in groundwater samples, beyond the concentrations of Ca^{2+} and Mg^{2+} ions. As RSC values increase, Ca^{2+} and Mg^{2+} ions in the soil precipitate in the form of CO_3^{2-}or HCO_3^-. This, in turn, leads to an elevation in the sodium content of the soil. Consequently, an increase in the rate of salt absorption on soil particles may lead to a sodium hazard. Consistent usage of waters with elevated levels of residual sodium carbonate has an immense effect on crop yield.

$$\mathrm{RSC} = (\mathrm{CO_3^{2-}} + \mathrm{HCO_3^-}) - (\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}}) \qquad (5)$$

where the ions are estimated in meq/L. Waters having RSC levels greater than 2.5 meq/L should not be used for irrigation, whereas those between 1.25 and 2.5 meq/L are questionable, while those below 1.25 meq/L are fit. Calculated RSC values for groundwater samples in the research region ranged from -125.98 to -16.62, with a mean of -52.54. All the groundwater samples in the categorization of groundwater for irrigation needs based on RSC values are less than one, suggesting that it's an acceptable category (**Table 2**).

3.2.3. Sodium percent (%Na) and Wilcox diagram

Sodium percentage (%Na) is often used as an indicator of water quality. it is calculated using equation (6).

$$\%\ \mathrm{Na^+} = \frac{(\mathrm{Na^+} + \mathrm{K^+})}{(\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + \mathrm{Na^+} + \mathrm{K^+})} 100 \qquad (6)$$

The total ionic concentrations are calculated in meq/L. Obviously, the majority of samples have Na% values within the range of 25.46 to 54.07, which corresponds to the categories of good (20%) and acceptable (0%). Elevated levels of Na^+ in water are unfavorable due to their ability to disperse soil aggregates, adsorb onto soil cation exchange sites, and reduce the permeability of soil (Pazand and Javanshir 2014; Sethy et al. 2016; Golchin and Azhdary Moghaddam 2016).

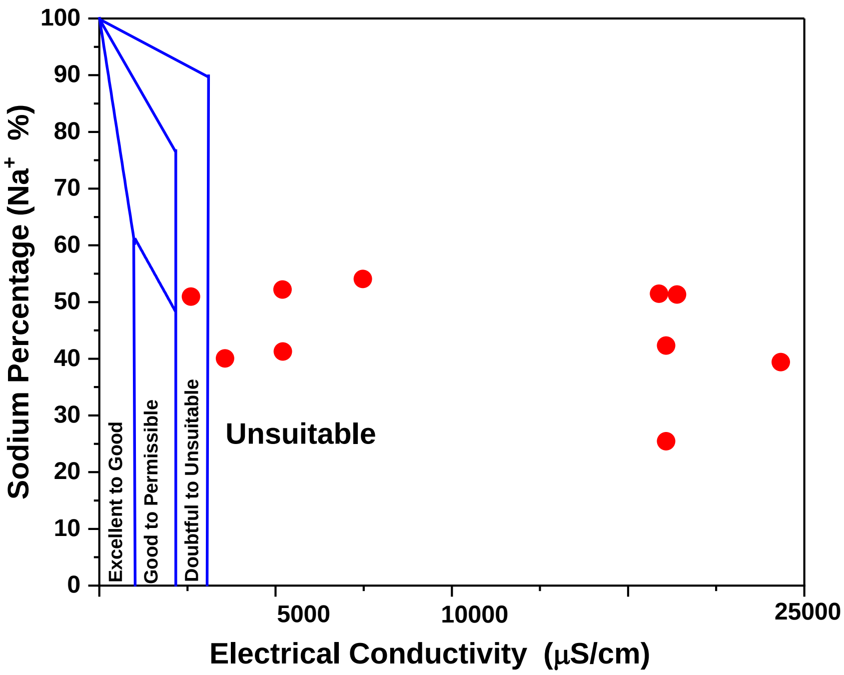

Figure 9. Classification of irrigation waters using Wilcox diagram

The Na% and EC plots in the Wilcox diagram are frequently used to evaluate the appropriate of water for irrigation purposes. As shown in Figure 9, 10% of the samples are considered to be hazardous or improper for irrigation. Whereas 90% of the water samples exhibit high electrical conductivity (EC) values, which rendering them unacceptable for irrigation of corps that requires low Na content and EC values (as shown in Table 2). However, such water may still be utilized for irrigating salt-tolerant plant species, such as halophytes (e.g., *Atriplex*, *Salicornia*) (FAO, 2018).

*3.2.4. **Permeability index (PI)***

The permeability index, as described by Doneen (1964), is used to evaluate the viability of groundwater for irrigation purposes. It is calculated using equation (7).

$$PI= \frac{Na + \sqrt{HCO_3}}{Ca+Mg+Na} \text{ x } 100 \qquad (7)$$

All concentrations are measured in meq/L. According to this indicator, water can be classified into three types. Class I and Class II water, which have a permeability of 75% or more, are suitable for irrigation. However, Class III water, with a maximum permeability of 25%, is not acceptable for irrigation. The groundwater in this study is categorised as class II based on the computed permeability index, that varies from 27.89 to 58.55% with an average of 47.64%. In light of this reasoning, Al-Wajh groundwater may be used for agricultural irrigation.

*3.2.5. **Potential salinity (PS)***

The potential salinity is another good parameter for the assessment of irrigation water quality (Doneen 1964). Adding a Cl concentration and 1⁄2 of a SO_4 concentration will yield the potential salinity as in equation (8).

$$PS= Cl + \frac{SO_4^{2-}}{2} \qquad (8)$$

where meq/L units are used to measure all ions. Water is deemed appropriate for irrigation if the PS value is below 3 meq/L. If the PS value exceeds 3 meq/L, the water is regarded improper for irrigation. Evedently, the water samples in this location exhibit inadequate quality for application in irrigation activities.

*3.2.6. **Kelly’s ratio (KR)***

Kelley's ratio is a useul index to evaluate the quality of groundwater for agricultural purposes. It is computed as using equation (9).

$$\mathrm{KR} = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}} \qquad (9)$$

Where all ions are measured in meq/L. According to Ayers and Westcot (1985), water with a Kelly's Ratio (KR) greater than 1 usually regarded asinadequate for irrigation, whereas water with a KR less than 1 is generally regarded as an acceptable. The results presented in Table 2 indicate that approximately 50% of the groundwater samples may be appropriate for irrigating various crops, while the remaining 50% are considered unsuitable for this purpose.

*3.2.7. **Corrosvity ratio (CR)***

CR is a good tool to identify the proper piping materials for water delivery. it is calculated using equation (10) (Ryzner 1944).

$$\mathrm{CR} = \frac{0.028\ \mathrm{Cl}^{-} + 0.021\ \mathrm{SO}_4^{2-}}{0.02(\mathrm{HCO}_3^{-} + \mathrm{CO}_3^{2-}} \qquad (10)$$

When the CR value of groundwater exceeds 1, it is necessary to use PVC pipes for its transportation, as metallic pipes have no capacity to tolerate the corrosive effects. However when the CR is less than 1, it is possible to transport groundwater through pipelines of any type (Mondal et al. 2016; Ekbal and Khan 2022). Water becomes more corrosive when it contain high proportions of chloride and sulphate. The CR values in the analysed area vary from 4.68 to 40.38, as indicated in Table 2. It is evident that only PVC pipes are appropriate for delivering this particular type of water.

4. Conclusion

The result of this investigation revealed that Ca^{2+} and Cl^{-} concentrations were the most abundant cation and anion in the analyzed groundwater samples. The proportion of strong acids (Cl^{-} and SO_4^{2-}) and alkaline earths (Ca2+ and Mg2+) is significantly higher than that of weak acids (HCO_3^{-} and CO_3^{2-}), which confirm the predominance of mixed Ca-Mg-Cl, Ca-Cl, and Na-Cl types. The presence of several types of rocks, particularly limestone, dolomitic limestone, and residual salts in sedimentary strata, seem to have great impact on the chemical composition of the groundwater sources in Al Wajh. Lithology plays a role for establishing the chemical composition of groundwater, both in Al Wajh and across Europe (Clemens et. al., 2010). The chemistry of water is influenced by lithological variables, weathering processes, revers ion exchange, and evaporation. The high concentrations of (Ca_2^{+} + Mg_2^{+})/HCO_3^{-} and (Ca_2^{+} + Mg_2^{+}) / (HCO_3^{-}+ SO_4^{2-}) suggest that both the dissolution of carbonates and evaporates play a role in the chemical composition of the water in the area of study. The assessment of groundwater, as conducted by the Wilcox and US categorization methods, revealed that the groundwater was was unsuitable for irrigation purposes. The elevated salinity levels render this water source unsuitable for direct consumption or certain agricultural uses. However, advanced treatment technologies, such as reverse osmosis and electrodialysis, can effectively reduce salinity to acceptable levels. In addition, mixing this groundwater with desalinated seawater (e.g., multi effect distillation (MED)) is a viable strategy to restore the essential ion balance, making it suitable for both human consumption and agriculture. This approach aligns with the objectives of Saudi Arabia's Vision 2030 by promoting sustainable water management and the diversification of water sources to enhance long-term water security. Certainly, by integrating innovative treatment solutions, the Kingdom is progressing toward reduced reliance on traditional water sources and enhanced water sustainability.

References

Abdullatif, O., Osman, M. (2019), Reservoir Heterogeneity and Quality of Wajh Formation: Outcrop Analog Study, Red Sea Region, Saudi Arabia. **1**, 1-5.

Ahmed, I., Nazzal, Y., Zaidi, F. K., Al-Arifi, N. S., Ghrefat, H., Naeem, M. (2015), Hydrogeological vulnerability and pollution risk mapping of the Saq and overlying aquifers using the DRASTIC model and GIS techniques, NW Saudi Arabia. *Environmental Earth Sciences*, **74**, 1303-1318.

Al-Amry, A. S. (2008), *Hydrogeochemistry and groundwater quality assessment in an arid region: a case study from Al Salameh Area, Shabwah, Yemen*, The 3rd International Conference on Water Resources and Arid Environments, The 1st Arab Water Forum.

Al-Bassam A M, Hussein T, Sharaf M A. (1997), Hydrochemical evaluation of the Umm-er-Radhuma Aquifer system, Saudi Arabia Hydrochemistry (Proceedings of the Rabat Symposium, April 1997), IAHS Publ no 244.

Al-Bassam, A. M. (2006), Evaluation of ground water quality in Al-Qassim area, Saudi Arabia, using cluster and factor analyses, *Kuwait Journal for Science and Engineering*, 33(2), 101-121.

Alfaifi, H. J. (2019), Combined graphical and geostatistical technique to determine the hydrochemical processes affecting groundwater chemistry in coastal areas, Western Saudi Arabia, *Arabian Journal of Geosciences*, **12**, 1-12.

Alhababy, A. M., Al-Rajab, A. J.(2015), Groundwater quality assessment in Jazan region, Saudi Arabia. Current. World Environment, **10**, 22-28.

Al-Shaibani, A. M.(2020), Lava fields as potential groundwater sources in Western Saudi Arabia. In Hydrology and Water Resources, CRC Press: pp 103-120.

AlSuhaimi, A.O., AlMohaimidi, K.M., Momani, K.A., (2019). Preliminary assessment for physicochemical quality parameters of groundwater in Oqdus Area, Saudi Arabia. Journal of the Saudi Society of Agricultural Sciences **18**, 22–31

American Public Health Association (APHA), (1998), Standard methods for the examination of water and wastewater, 20th edn Washington

Ayers, R. S., and Westcot, D.W. (1985), *Water quality for the irrigation* (p. 97), Irrigation drainage paper 29, FAO United Nations, Rome.

Baggazi, H. M., AlKashghari, W. A., Elfakharani, A., Matsah, M., El-Shafei, M. K. (2019), Northern Arabian Shield shear zones: strain analysis comparison. *Arabian Journal of Geosciences*, **12** , 1-9.

Bamousa AO, Matar SS, Daoudi M, Al-Doaan, MI (2013), Structural and geomorphic features accommodating groundwater of Al-Madinah City, Saudi Arabia, Arabian Journal of Geosciences, **6**, 3127–3132

Bokhari, A. Y., & Khan, M. A. (1992). Deterministic modelling of Al-Madinah Al-Munawarah groundwater quality using lumped parameter approach. *Earth Sciences*, **5**, 89–107.

Brima, E. I., AlBishri, H. M.(2017), Major and trace elements in water from different sources in Jeddah city, KSA. Arabian Journal of Geosciences, **10**, 1-8.

Brown, G. F., Schmidt, D. L., Huffman Jr, A. C. (1989), *Geology of the Arabian Peninsula, shield area of western Saudi Arabia*, 2330-7102, US Geological Survey.

Choi, B.Y., Yun, S.T., Yu, S.Y., Lee, P.K., Park, S.S., Chae, G.T., and Mayer, B. (2005), Hydrochemistry of urban groundwater in Seoul, South Korea: effect of land-use and pollutant recharge. *Environmental Geology* **48**, 979–990.

Clemens R, Manfred B, David B, et al (2010), Geochemistry of European Bottled Water. E. Schweizwrbart Science Publishers. 1-268.

Corteel, C., Dini, A., Deyhle, A. (2005), Element and isotope mobility during water–rock interaction processes. Physics and Chemistry of the Earth, Parts A/B/C, **30** (17-18), 993-996.

Davis, S. N., and. De Weist R. J. M. (1966), Hydrogeology, 463 pp., John Wiley, New York.

De Wiest R J. (1966), On the storage coefficient and the equations of groundwater flow. Journal of Geophysical Research,**71**, 1117-1122.

DeNicola, E., Aburizaiza, O. S., Siddique, A., Khwaja, H., Carpenter, D. O. (2015), Climate Change and Water Scarcity: The Case of Saudi Arabia. Annals of Global Health, **81**, 342-353.

Dixon, W., and Chiswell, B. (1992), The use of hydrochemical sections to identify recharge areas and saline intrusions in alluvial aquifers, southeast Queensland, Australia. *Journal of Hydrology*, **130**, 299–338.

Doneen, L. D. (1964), *Notes on water quality in agriculture*. Published as a water sciences and engineering paper 4001. Dept. of Water Sciences and Engineering, University of California.

Drever, J.I. (1997), The geochemistry of natural waters (3rd ed.), New Jersey: Prentice Hall,436

Eaton, F. M. (1950), Significance of carbonate in irrigation water. *Soil Science,* **69**, 123–133.

Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Bath, A.H, Morganjones, M., Andrews, J.N..(1987), Baseline geochemical conditions in the Chalk aquifer, Berkshire, UK.: a basis for groundwater quality management. *Applied Geochemistry, 2,* 251–274.

Ekbal, E., and Khan, T. A. (2022), Hydrogeochemical Characterization of Groundwater Quality in Parts of Amroha District, Western Uttar Pradesh, India. *HydroResearch,* **5**, 54-70.

Elango, L., and Kannan, R. (2007), Rock–water interaction and its control on chemical composition of groundwater. *Developments in environmental science*, **5**, 229-243.

FAO. (2018). Handbook for saline soil management. Food and Agriculture Organization of the United Nations and Lomonosov Moscow State University. pp 66-70.

Fisher, R. S., and Mulican III, W. F. (1997), Hydrochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the Northern Chihuahuan desert, TransPecos, Texas, USA. Hydrogeology Journal, **5**(2), 4–16.

Gao, X., Wang, Y., Li, Y., and Guo, Q. (2007), Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. *Environmental Geology*, **53**, 795-803.

Garcia, M. G., del v. Hidalgo, M., and Blessa, M. A. (2001), Geochemistry of groundwater in the alluvial plain of Tucuman province, Argentina. *Hydrogeology Journal,* **9**, 597–610.

Golchin, I., and Azhdary Moghaddam, M. (2016), Hydro-geochemical characteristics and groundwater quality assessment in Iranshahr plain aquifer, Iran. *Environmental Earth Sciences*, ***75***, 1-14.

Ghimire M, Kayastha S P, Regmi T, et al.(2023), Hydro-chemical characterisation and quality assessment of shallow groundwater in parts of the Kathmandu Valley, Nepal. Physics and Chemistry of the Earth, Parts A/B/C, **129**: 103349.

Gibbs, R J. (1970), Mechanisms controlling world water chemistry Science, **170**: 1088–1090

Golchin, I., and Azhdary Moghaddam, M. (2016), Hydro-geochemical characteristics and groundwater quality assessment in Iranshahr plain aquifer, Iran. *Environmental Earth Sciences*, *75*, 1-14.

Golditch, S. S. (1938), A study in rock weathering. *The Journal of Geology*, **46**, 17.

Hem, J. D. (1989). *Study and interpretation of the chemicalcharacteristics of natural water. U.S.G.S. Water-supply paper* (Vol. 2254). Washington DC: US Government Printing Office

Jalali, M. (2005), Major ion chemistry in the Bahar area, Hamadan, western Iran. *Environmental Geology*, **47**, 763–772.

Jalali, M. (2009), Geochemistry characterization of groundwater in an agricultural area of Razan, Hamadan, Iran. *Environmental Geol*ogy, **56**:1479–1488.

Johnson, P., Andresen, A., Collins, A., Fowler, A., Fritz, H., Ghebreab, W., Kusky, T., Stern, R. (2011), Late Cryogenian–Ediacaran history of the Arabian–Nubian Shield: a review of depositional, plutonic, structural, and tectonic events in the closing stages of the northern East African Orogen, *Journal of African Earth Sciences***, 61**, 167-232.

Kumar, S. K., Rammohan, V., Sahayam, J. D., and Jeevanandam, M. (2009), Assessment of groundwater quality and hydrogeochemistry of Manimuktha River basin, Tamil Nadu, India. *Environmental Monitoring and Assessment,* **159**, 341–351.

Magaritz, M., Nadler, A., Koyumdjisky, H., and Dan, N. (1981). The use of Na/Cl ratio to trace solute sources in a semiarid zone. *Water Resources Research,* **17**, 602–608.

Maiti T.C. (1982), The dangerous acid rain. Science Report **9**, 360–363

Majumdar, D., and Gupta, N. (2000), Nitrate pollution of groundwater and associated human health disorders. *Indian Journal of Environmental Health,* **42,** 28–39

Mallick, J., Kumar, A., Almesfer, M.K., Majed Alsubih, Singh, C.K., Ahmed, M., Khan, R.A. (2021), An index-based approach to assess groundwater quality for drinking and irrigation in Asir region of Saudi Arabia. *Arabian Journal of Geosciences* 14, 157, 1-20.

Masoud, A., Kehail, A.A., (2024), Evaluation of the physical parameters of water obtained from some groundwater sources of Tabuk city, Kingdom Saudi Arabia. *International Journal of Science and Research Archive,* 12, 1346–1350.

Meybeck, M. (1987), Global chemical weathering of surficial rocks estimated from river dissolved loads. *American journal of science, **287***, 401-428.

Mohan, R., Singh, A. K., Tripathi, J. K., and Chowdhary, G. C. (2000). Hydrochemistry and quality assessment of groundwater in Naini industrial area, Allahabad District, Uttar Pradesh. *Geological Society of India, 55,* 77-89.

Mondal, N.C., Tiwari, K.K., Sharma, K.C., Ahmed, S., (2016), A diagnosis of groundwater quality from a semiarid region in Rajasthan, India. *Arabian Journal of Geosciences,* **9**, 1–22 article 602.

Muhammad, N., Hussain, I., Ali, A., Noureen, L., He, Q., Subhani, Q.,& Zhu, Y. (2024). Ion chromatography: A comprehensive review of sample preparation methods for analysis of halogens and allied nonmetals in critically challenging inorganic matrices. *Journal of Chromatography A,* 1734, 465311.

Muhammad, N., Zia-ul-Haq, M., Ali, A., Naeem, S., Intisar, A., Han, D., & Wei, B. (2021). Ion chromatography coupled with fluorescence/UV detector: A comprehensive review of its applications in pesticides and pharmaceutical drug analysis. *Arabian Journal of Chemistry*, 14, 102972.

Pazand, K., and Javanshir, A. R. (2014), Rare earth element geochemistry of spring water, north western Bam, NE Iran. *Applied Water Science,* **4**, 1-9.

Piper, A. M. (1944), A graphic procedure in the geochemical interpretation of water-analysis. *Tranansactions American Geophysical Union*, **25**, 914–928.

Ragunath, H.M. (1987), *Groundwater* (p. 563), New Delhi: Wiley.

Rajmohan, N., and Elango, L. J. E. G. (2004), Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. *Environmental Geology*, **46**, 47-61.

Reghunath, R., Murthy, T. S., Raghavan, B. (2002), The utility of multivariate statistical techniques in hydrogeochemical studies: an example from Karnataka, India. Water research, **36**, 2437-2442.

Rahman M M, Haque T, Mahmud A, et al. (2023),. Drinking water quality assessment based on index values incorporating WHO guidelines and Bangladesh standards. Physics and Chemistry of the Earth, Parts A/B/C, **129**, 103353.

Rajmohan N, Elango L J .E G.(2004), Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins Southern India. *Environmental Geology*, **46**, 47-61.

Reimann C, Birke M (2010), Geochemistry of European bottled water.

Richards L A (1954), Diagnosis and improvement of saline and alkali soils. LWW. **78**, 154.

Ryznar, J. W. (1944). A new index for determining amount of calcium carbonate scale formed by a water. *Journal-American Water Works Association*, **36**, 472-483.

Sami, K. (1992), Recharge mechanisms and geochemical processes in a semi-arid sedimentary basin, Eastern cape, South Africa. *Journal of Hydrology*, **139**, 27–48.

Sanchez-Perez, J.M., and Tremolieres, M. (2003), Change in groundwater chemistry as a consequence of suppression of floods: The case of the Rhine floodplain. *Journal of Hydrology*, **270**, 89–104.

SASO (Saudi Arabian Standards Organization), (1984), *Bottled and Unbott1ed Drinking Water*, SSA 409/1984, 2nd ed., 1996-03-13, ISSN: 1319-2302, Available from: SASO Information Center, P.O.Box.3437, Riyadh, 11471, Saudi Arabia, pp.1 -8.

Scholler, H. (1977). *Geochemistry of groundwater*. In Groundwater studies-An International guide for research and practice (Ch. 15, pp. 1–18). Paris:UNESCO.

Sethy, S. N., Syed, T. H., Kumar, A., and Sinha, D. (2016), Hydrogeochemical characterization and quality assessment of groundwater in parts of Southern Gangetic Plain. *Environmental Earth Sciences*, **75**(3), 1-15.

Shahid SA, Mahmoudi H (2014), National strategy to improve plant and animal production in the United Arab Emirates. Soil and water resources Annexes.

Sharaf, M. A. M., (2013), Major elements hydrochemistry and groundwater quality of Wadi Fatimah, West Central Arabian Shield, Saudi Arabia. Arabian Journal of Geosciences, **6**, 2633-2653.

Shraim, A., ALSuahimi, A., AlMuzaini, K. (2013). Quality Assessment of Groundwater of Almadinah Almunawarah City. Global Nest Journal 15(3), 374–383.

Singh, C. K., Rina, K., Singh, R., Shashtri, S., Kamal, V., Mukherjee, S. (2011), Geochemical modeling of high fluoride concentration in groundwater of Pokhran area of Rajasthan, India. Bulletin of Environmental Contamination and Toxicology, **86**, 152-158.

Srinivasamoorthy, K., Nanthakumar, C., andVasanthavigar, M. (2011), Groundwater quality assessment from a hard rock terrain, Salem district of Tamilnadu, India. *Arabian Journal of Geosciences*, **4,** 91-102.

Stallard R F, Edmond J M (1983), Geochemistry of the Amazon: 2 The influence of geology and weathering environment on the dissolved load. Journal of Geophysical Research: Oceans, **88**, 9671-9688

Subba Rao, N., Surya Rao, P., Venktram Reddy, G., Nagamani, M., Vidyasagar, G., and Satyanarayana, N.L.V.V. (2012), Chemical characteristics of groundwater and assessment of groundwater quality in Varaha River Basin, Visakhapatnam District, Andhra Pradesh, India. *Environmental Monitoring and Assessment,* **184**, 5189–5214.

Toumi, N., Hussein, B.H.M., Rafrafi, S., and kassas, N. (2013),. Dissolved nitrogen Survey in Groundwater Resources in Al-Ula village, Madina El Monawara, Saudi Arabia. *CATRINA*, **8**, 37 -42.

Toumi, N., Hussein, B. H., and Rafrafi, S. (2015). Groundwater quality and hydrochemical properties of Al-Ula region, Saudi Arabia. *Environmental Monitoring and Assessment*, **187**, 1-16.

USSL (United States Salinity Laboratory), (1954), Diagnosis and improvement of saline and alkaline soils. Agriculture Handbook No. 60 USDA, p 160

Venugopal, T., Giridharan, L., Jayaprakash, M., and Periakali, P. (2009). Environmental impact assessment and seasonal variation study of the groundwater in the vicinity of River Adyar, Chennai, India. *Environmental monitoring and assessment*, **149**, 81-97.

Wilcox, LV (1955), Classification and Use of Irrigation Water US Department of Agriculture, Circular 969, Washington DC.

World Health Organization (WHO), (2011), Guidelines for quality, 4th edn. In: Geneva 541

Zaman, M., Shahid, S. A., and Heng, L. (2018), Irrigation water quality. In *Guideline for salinity assessment, mitigation and adaptation using nuclear and related techniques* (pp. 113-131). Springer, Cham.

Zilberbrand, M., Rosenthal, E., and Shachnai E. (2001), Impact of urbanization on hydrochemical evolution of groundwater and unsaturated-area gas composition in the coastal city of Tel Aviv, Israel. *Journal Contaminant Hydrology,* **50**,175–208