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Hydrogeochemical Characteristics and Quality Assessment of Groundwater in Semi-Arid Region of District Mianwali, Pakistan: A Multivariate Statistics Approach

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ABSTRACT

Hydrogeochemical characterization and groundwater quality assessment in terms of suitability for domestic and irrigation purposes of Piplan area, district Mianwali has been investigated. Three major hydrogeochemical facies (Ca-Mg-HCO_3 > Na-HCO_3 > Ca-Mg-Cl) are identified by Piper's diagram. The dominant hydrogeochemical facies, Ca-Mg-HCO_3 suggested fresh recharge to groundwater. To recognize the defining processes of hydrogeochemistry, Gibbs diagram plays a vital role by ascertaining the water-rock interaction; whereas, silicate weathering is recognized as a primary source of mineral dissolution with dolomite ($CaMg(CO_3)_2$) as the major geochemical phase. The physico-chemical and chemical parameters such as pH, EC, TDS, Ca, Mg, Na, K, HCO_3, Cl, SO_4 and NO_3 were employed to substantiate groundwater quality. Overall water quality of the study area is found admissible in comparison to World Health Organization (WHO) and Pakistan Standard Quality Control Authority (PSQCA) standards for drinking as well as domestic consumption. On the other hand, quality of irrigation water is generally well below the permissible limits of irrigation suitability indices such as sodium percentage (Na%), sodium adsorption ratio (SAR), permeability index (PI) and Kelly's ratio (KR), except the residual sodium carbonate (RSC) and magnesium hazard (MH). Principal component analysis (PCA) revealed mineral dissolution and rock weathering as the distinctive phenomena controlling groundwater chemistry and groundwater pollution by anthropogenic sources.

1. Introduction

Groundwater is the most valuable natural resource; it is the primary source of water used for drinking, agricultural, industrial and environmental activities, etc. [1]. In the last few decades, irrigation water demand has increased many folds all around the world. Globally, around 43% of the groundwater is utilized for agricultural irrigation and this will further increase by 14% by 2030 [2]. To fulfill the ever-rising water requirements of the growing population, excessive groundwater abstraction has resulted in depletion and deterioration of underground aquifers [3-6].

Pakistan is facing severe challenges associated with the sustainability of groundwater resources, owing to maladministration and overexploitation of groundwater, which are the key factors that lead to excruciating damage to this valuable natural resource. The heavy abstraction of groundwater has not only threatened the water quality but is also responsible for declining agricultural yield [7]. Over a span of fifty years (1960 to 2010), the share of groundwater use for irrigation has increased from just 8% to more than 50% [8]. Currently, more than 50% of the irrigation and 70% of the drinking water demand is being fed by groundwater abstraction. Consequently, excessive pumping has not only caused a drawdown of the water table and salinization of freshwater resources in shallow unconfined aquifers but also proved to be detrimental to groundwater in terms of pollution, which is the root cause of numerous environmental problems [9-12]. Although, agricultural irrigation has a predominant role towards increased crop productivity in Pakistan and especially in semi-arid areas with typically high evapotranspiration rates [13] and erratic precipitation pattern, but on the other hand it has adversely affected the soil health and productiveness by altering the natural balance of dissolved salts of soil [14]. The suitability of groundwater for irrigation purposes mainly depends on its salt contents. Elevated levels of dissolved salts in irrigation water lead to sodic soil and salinity [15, 16]. Moreover, salinity is not only detrimental to soil fertility but it also penetrates the shallow aquifers transforming fresh groundwater resources to unsuitable for agricultural and domestic use [17].

Numerous studies were carried out in different areas of Punjab, Pakistan, focused on overall declining pattern in groundwater quality in all the study areas in comparison with the Pakistan Standard Quality Control Authority (PSQCA) and World Health Organization (WHO) standards [18-20]. These investigations concluded that deterioration of groundwater quality was mainly attributed to the infiltration of effluents originating from municipal as well as the industrial waste and agricultural runoff.

Groundwater quality assessment is inevitable for safe and sustainable exploitation of freshwater resources in arid and semi-arid areas. So far, the selected study area has not been investigated regarding hydrogeochemical characterization and groundwater quality assessment. Therefore, the present study is carried out to identify various hydrogeochemical processes and assessment of groundwater quality.

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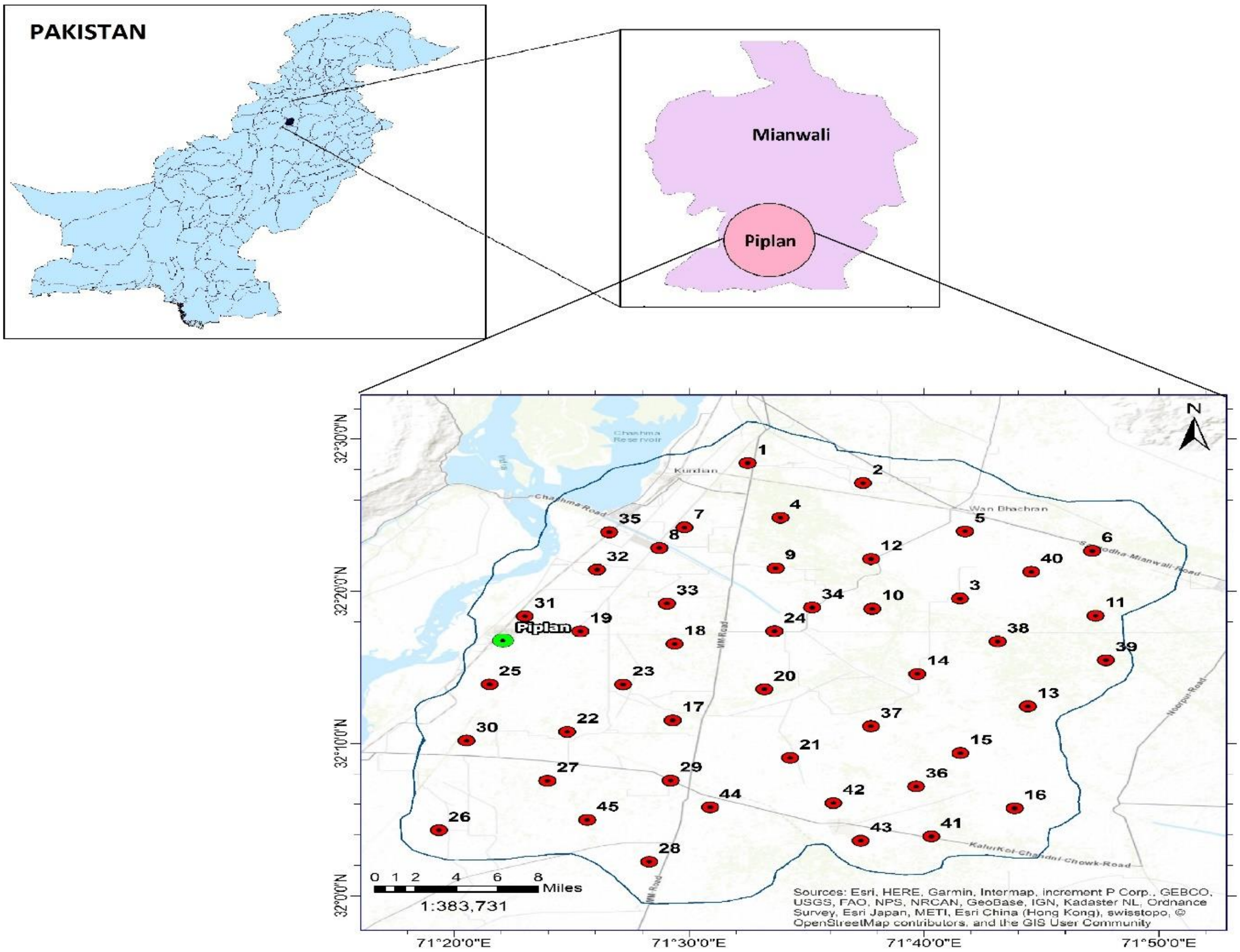

Fig. 1: Map of the study area.

2. Materials and Methods

2.1 Study area

The study area (Fig. 1) of Tehsil Piplan, District Mianwali comprises an area of about 2000 km^2. It is situated between geographical coordinates from latitude 32°2' N to 32°28' N and longitude 71°18' E to 71°44' E. It has a semi-arid climate with a long hot summer season and cold dry winters. Summer lasts from May to September, the hottest month being June with average temperatures of 42 °C, while the winter season spans from November to February, January being the coldest month with average temperatures of 11.7 °C. The mean annual rainfall for the last two decades was around 385 mm. Agriculture is the economic backbone of the whole district, which largely depends on groundwater exploitation and canal irrigation system to fulfill its water demand.

2.1.1 Geological and hydrogeological settings

The study area comprises a portion of the upper Thal Doab, interfluve between the rivers Indus and Jhelum. The alluvial deposits of quaternary period are the pronounced geological feature, which are heterogeneously distributed in perpendicular as well as horizontal direction. Furthermore, the drilling data elucidate that sand formations are in the form of consecutive layers of silt and clay of varying thickness [21].

2.2 Water sample collection and assessment

Two sets of groundwater samples were collected twice a year (dry and rainy season) from 45 wells (shallow & deep) in 2019. All the samples were kept in polyethylene bottles and stored at 4 ^{o}C. Physico-chemical parameters such as temperature, pH and electrical conductivity were measured in situ. Elemental concentrations of sodium, potassium, calcium and magnesium were analyzed by atomic absorption spectrophotometer (iCE-3000 AAS, Thermo scientific). Bicarbonate and Chloride were analyzed by acid titration and silver nitrate ($AgNO_3$) titration method, respectively. Sulphate was determined by the $BaCl_2$ turbidity method using a UV/Visible spectrophotometer (CE-7500, Cecil). The analytical procedures were followed as suggested by the American Public Health Association [22].

Principle component analysis was performed using XLSTAT software (v 2017.1) [23] to illustrate and summarize the variability in the data set in terms of inter-correlation among all the variables. Moreover, Piper and Wilcox's diagram were prepared through Aqua-Chem (version 2011.1) [24], to interpret hydrogeochemical facies and to classify irrigation suitability of groundwater. Whereas, saturation indices were calculated through geochemical modeling program PHREEQC (version 2.18) [25].

To evaluate irrigation water suitability, various parameters such as Na%, sodium adsorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), Kelly's ratio (KR) and magnesium hazard (MH) were used. These parameters were calculated using the following equations [26].

$$\mathrm{Na\%} = \frac{\mathrm{Na}^{+}}{(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}+\mathrm{Na}^{+}+\mathrm{K}^{+})} \times 100 \qquad (1)$$

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

$$\mathrm{RSC} = (\mathrm{CO}_3^{2-} + \mathrm{HCO}_3^{-}) - (\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}) \qquad (3)$$

$$\mathrm{PI} = \frac{(\mathrm{Na}^{+} + \sqrt{\mathrm{HCO}_3^{-}})}{(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}+\mathrm{Na}^{+}+\mathrm{K}^{+})} \times 100 \qquad (4)$$

$$\mathrm{KR} = \frac{\mathrm{Na}^{+}}{(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+})} \qquad (5)$$

$$\mathrm{MH} = \frac{\mathrm{Mg}^{2+}}{\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}} \times 100 \qquad (6)$$

3. Results and Discussion

3.1 Water quality for drinking

The results for physicochemical parameters such as pH, electrical conductivity (EC) and TDS are shown in Table 1. The pH value varies from 7.40 to 8.46 with a mean value of 7.92. The EC and TDS values range from 254 to 1305 µS/cm with an average value of 720 µS/cm and 165 to 848 mg/l with a mean value of 468 mg/l, respectively. The EC and TDS data suggest the fresh to slightly saline water type, which is suitable for drinking purposes. The values of physicochemical parameters are found well within the guidelines prescribed by WHO and PSQCA [27].

3.2 Groundwater chemistry

The evolution of groundwater chemistry is based on interaction among various dissolved constituents in an aquifer. Major cations such as Ca^{2+} range from 6–50 mg/l (mean value of 30 mg/l), $\mathrm{Mg}^{2+}$from 9–71mg/l (mean value of 34 mg/l), Na^{+} from 9–158 mg/l (mean value of 46 mg/l), and K^{+} from 3–22 mg/l (mean value of 10 mg/l) as shown in Table 1. The cation abundance reveals the following pattern, $\mathrm{Na}^{+} > \mathrm{Mg}^{2+} > \mathrm{Ca}^{2+} > \mathrm{K}^{+}$, with sodium emerging as a dominant cation, which indicates silicate weathering and ion exchange processes during the infiltration of surface water. On the other hand, cationic concentrations indicate that all groundwater samples are well within the permissible limit for Ca^{2+}, Mg^{2+} and Na^{+}. However, a few samples are beyond the permissible limit of potassium (12 mg/l), suggesting the weathering of potassium silicate or use of potassium fertilizer might be the source of higher concentrations. Intake of high concentration of potassium may lead to substantial health impacts in individuals with kidney disease or other diseases, such as heart disease, hypertension and diabetes [28].

Among the anions, bicarbonate is the most abundant ion in the groundwater with concentration range from 119 to 413 mg/l with an average value of 278 mg/l. While, the concentration of chloride was observed from 14 to 80 mg/l with a mean of 34 mg/l. Sulphate ranges from 15 to 151 mg/l with an average value of 53 mg/l, whereas the nitrate covers a range of values from 3.6 mg/l to 48.4 mg/l with an average of 17 mg/l. The order of anion abundance is $\mathrm{HCO}_3^{-} > \mathrm{SO}_4^{2-} > \mathrm{Cl}^{-} > \mathrm{NO}_3^{-}$. The abundance of bicarbonate in groundwater is attributed to the weathering of carbonates and silicates. Moreover, the secondary abundance of sulphate ion suggests the contribution by oxidation of sulphite [29].

Table 1: Summary of groundwater chemistry.

Parameter	Min	Max	Average	WHO	PSQCA
pH	7.4	8.46	7.92	6.5-8.5	6.5-8.5
EC (µS/cm)	254	1305	720	1500	1500
TDS (mg/l)	165	848	468	1500	1000
HCO_3^{-} (mg/l)	119	413	278	500	-
Cl^{-} (mg/l)	14	80	34	250	250
SO^{2-}_4 (mg/l)	15	151	53	250	250
NO^{-}_3 (mg/l)	3.6	48.4	17	50	50
Ca^{2+} (mg/l)	6	50	30	200	-
Mg^{2+} (mg/l)	9	71	34	150	-
Na^{+} (mg/l)	9	158	46	200	-
K^{+} (mg/l)	3	22	10	12	-

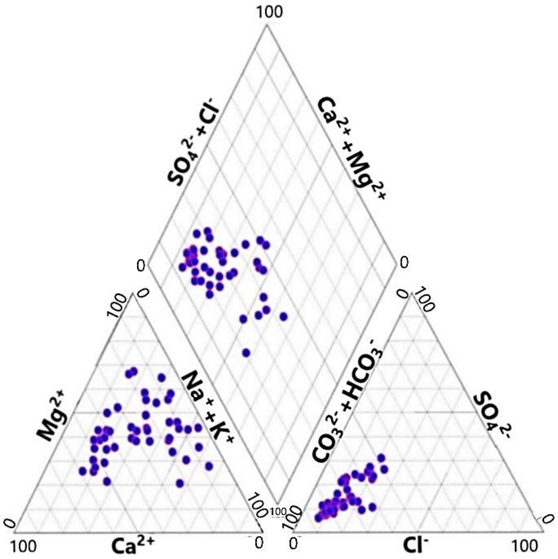

Fig. 2: Hydrogeochemical classification of groundwater.

3.3 Hydrogeochemical characteristics of groundwater

Piper trilinear diagram is widely used to differentiate between various hydrogeochemical facies by incorporating geochemical reactions occurring in the underlying aquifer (Fig. 2). Piper diagram [30] has distinguished and classified all the groundwater samples into three major water types mainly Ca-Mg-HCO_3, Na-HCO_3 and Ca-Mg-Cl.

Samples located in the lower right triangle, reflect HCO_3^{-} type water, which constitutes 95% of the total anion load, except two samples with no particular type. The diamond shape of trilinear diagram illustrates that about 85% of the groundwater samples are of Ca-Mg-HCO_3 type, 10% are of

$Na\text{-}HCO_3$ type and about 5% mixed Ca-Mg-Cl type water. The dominant $Ca\text{-}Mg\text{-}HCO_3$ type not only suggests fresh recharge to the groundwater but also specifies the dissolution of calcite or dolomite minerals. Moreover, $Na\text{-}HCO_3$ type water designates weathering of silicate rocks or ion exchange during water infiltration through the subsurface soil [31].

3.4 Origin of groundwater mineralization

3.4.1 Binary diagram

To identify the dominant mineral in the rock weathering process, bivariate plots of Ca^{2+}, Mg^{2+}, HCO_3^-, Na^+, K^+ and Cl^- were used previously [32, 33].

The ratio of $(Na^+ + K^+)/Cl^-$ was used as an indicator for silicate weathering, where $(Na^+ + K^+)/Cl^- > 1$ indicates Na^+ ion are principally liberated by silicate weathering and $(Na^+ + K^+)/Cl^- = 1$ indicates halite dissolution [34]. The binary diagram elucidates (Fig. 3a) that most of the groundwater samples have $(Na^+ + K^+)/Cl^-$ ratio > 1, which stipulates that silicate weathering is the primary source of Na^+ and K^+ ions in the groundwater.

Moreover, the graph of $(SO_4^{2-} + HCO_3^-)$ versus $(Ca^{2+} + Mg^{2+})$ demonstrates that Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} are mainly derived from the dissolution of either calcite or dolomite minerals. The bivariate plots (Fig. 3b) show that all the samples are closed or above the standard line (1:1), which indicates silicate weathering as the dominant source of ions (Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^-) in the groundwater system [35]. For better understanding of participating ions in silicate weathering process, chemical equation, Eq. (7), is given as:

$$(\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Na}^{+}, \mathrm{K}^{+})\mathrm{Silicates} + H_2\mathrm{CO}_3 \rightarrow H_4\mathrm{SiO}_4 + \mathrm{HCO}_3^- + \mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+} + \mathrm{Clay} \tag{7}$$

3.4.2 Gibbs diagram

Comprehension of the interrelationship between water composition and their respective hydrogeochemical origin provides a preferential role of various processes such as evaporation, rock-water interaction and precipitation. Gibb's diagram [36] is used to distinguish and identify the predominant process controlling the geochemical formation of the underground aquifer. It is evident from Fig. 4a that all the groundwater samples exhibit water-rock interaction as a primary phenomenon, which illustrates the chemical weathering of rock-forming minerals as well as its impact on groundwater. The quality of groundwater is markedly affected by rock-water interaction. The evaporation as a secondary process (Fig. 4b) also contributes considerably regarding hydrogeochemical formations. Thus, Gibbs diagram illustrates that groundwater chemistry is fundamentally controlled by complex geochemical mechanisms [37].

3.4.3 Hydrogeochemical modeling

Saturation index (SI) is widely used to recognize the different mineral phases, whether dissolved, soluble or at equilibrium in water at a particular physical condition [38].

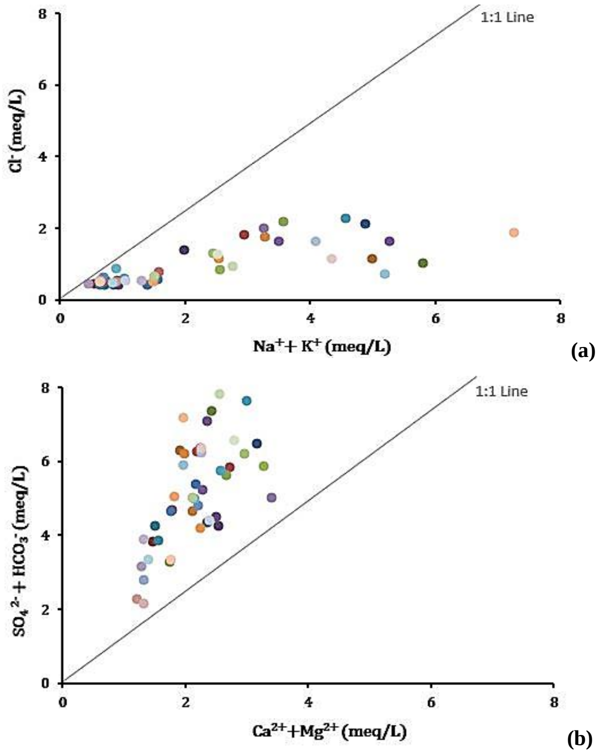

Fig. 3: Bivariate plots for groundwater mineralization processes (a) Cl vs Na+K plot, (b) SO_4+HCO_3 vs Ca+Mg plot.

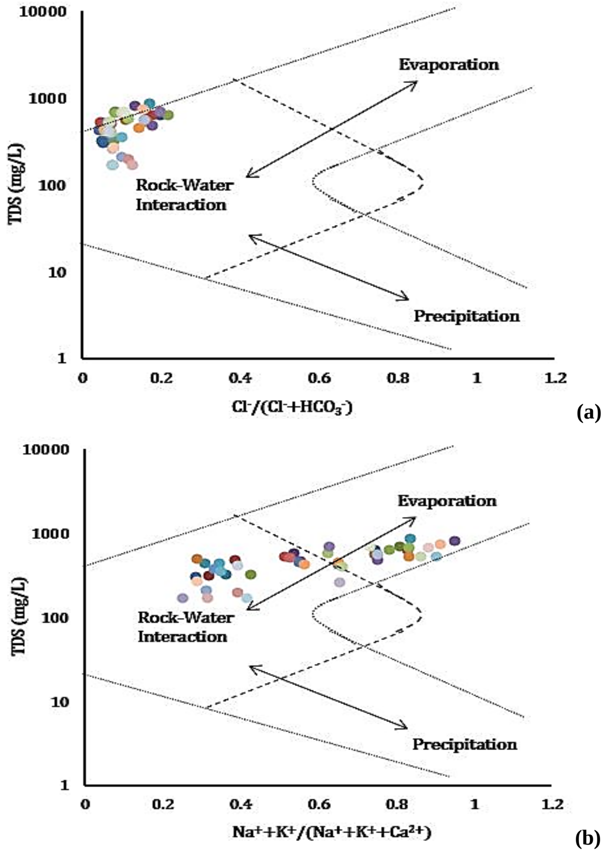

Fig. 4: Gibbs diagram (a) TDS vs Cl/Cl+HCO_3 plot, (b) TDS vs Na+K/(Na+K+Ca) plot.

The output data comprises either positive, negative or a zero value for a particular mineral. The positive value of SI represents precipitation, negative denotes dissolution and zero means the mineral is at chemical equilibrium corresponding to water phase. The mineral facies including gypsum, anhydrite, calcite, dolomite and halite were chosen based on the analytical results of groundwater quality. The positive values (Table 2) of dolomite ($CaMg(CO_3)_2$) with SI (4.61) demonstrate its dominant contribution towards the weathering process, while rest of the chemical phases contributed insignificantly as compared to dolomite; calcite (SI = 2.02), gypsum (SI = 0.25) and halite (SI = -5.57). The mechanism of dolomite dissolution is illustrated by Eq. (8).

$$\mathrm{CaMg(CO_3)_2} + 2\,\mathrm{CO_2} + 2\,\mathrm{H_2O} \leftrightarrow \mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + 4\mathrm{HCO_3^-} \qquad (8)$$

Table 2: Saturation index.

Phase	SI**	log(IAP)	log K (298K,1atm)
Anhydrite	-0.05	-4.33	-4.28
Calcite	2.02	-6.06	-8.48
Halite	-5.57	-4.00	1.57
Dolomite	4.61	-12.48	-17.09
Gypsum	0.25	-4.34	-4.58

3.5 *Suitability of groundwater for irrigation*

3.5.1 *Sodium adsorption ratio (SAR)*

Sodium Adsorption Ratio (SAR) is used to estimate the potential of sodium accumulation in the unsaturated soil zone owing to extensive use of sodic water [39]. The irrigation suitability of groundwater samples with respect to SAR has been evaluated using Eq. (2). Based on salinity and alkalinity risks, samples were further classified under distinct irrigation categories. The SAR value ranging from 6 to 9, will cause permeability problems on shrinking and swelling types of clay soils, when used for irrigation purpose [40].

Fig. 5 elucidates the classification of groundwater based on their SAR and EC values. Groundwater has been categorized into two types: C2S1 and C3S1. C2S1 represents the type of groundwater suitable for irrigation of semi tolerant crops; whereas, C3S1 type can be suitably used for irrigation of all soil types, however with a developmental risk of exchangeable sodium.

3.5.2 *Sodium percentage (Na%)*

Irrigation water with excess sodium concentration preferentially displaces Ca^{2+} and Mg^{2+} ions during infiltration through the soil, which reduces soil permeability and eventually leads to poor internal drainage [41]. Sodium percentage (Na%) is calculated using Eq. (1).

Na% for all the groundwater samples ranges from 16.32% to 74.21%. It is evident from Table 3 that 58% of samples are characterized as good to excellent for irrigation purpose; whereas the remaining 29 % are permissible and 13% are doubtful for irrigation. On the other hand, Wilcox diagram [42] (Fig. 6) illustrates that 67% of the samples range from "Excellent to Good", while the remaining 33% fall under "Good to Admissible" class. Therefore, groundwater is broadly categorized as excellent to permissible for irrigation use with respect to sodium percent.

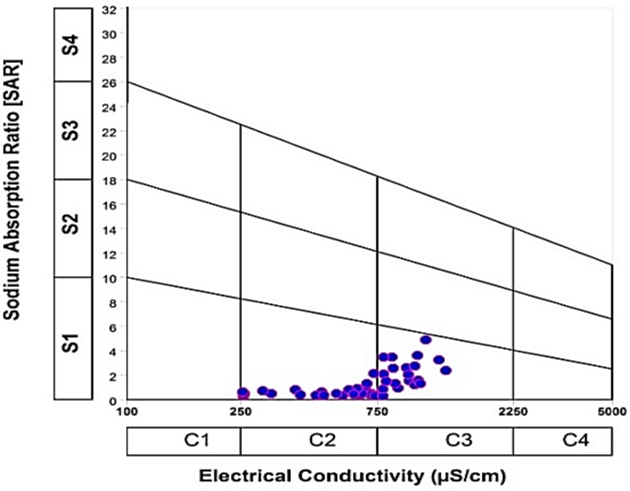

Fig. 5: US salinity diagram for assessment of irrigation water quality.

Table 3: Classification of groundwater quality based on sodium percentage.

Sodium (Percent)	Water Quality	No. of Samples (%)
< 20	Excellent	4 (9%)
20 - 40	Good	22 (49%)
40 - 60	Permissible	13 (29%)
60 - 80	Doubtful	6 (13%)
> 80	Unsuitable	-

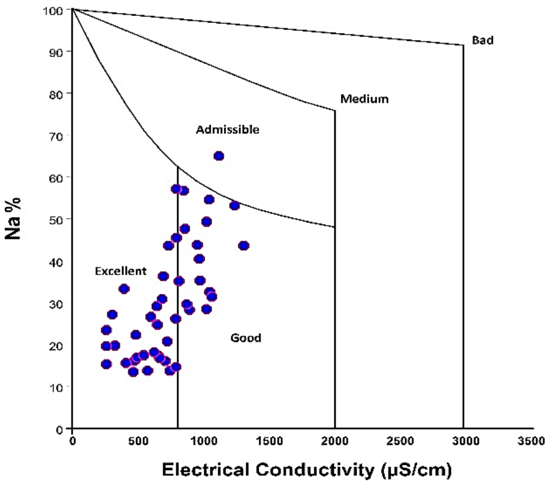

Fig. 6: Suitability of irrigation water, based on EC and Na%.

3.5.3 Residual sodium carbonate (RSC)

Residual sodium carbonate (RSC) is another important parameter used for the classification of groundwater in terms of irrigation suitability [43]. It measures the relative concentration of carbonate and bicarbonate ions in contrast to the abundance of calcium and magnesium ions. Since, elevated level of former ions in groundwater give rise to precipitation of calcium and magnesium as calcium and magnesium carbonates, which resultantly increase the relative amount of sodium in groundwater as sodium carbonate. Consequently, the presence of excess sodium carbonate in irrigation water not only reduces the soil fertility but is also detrimental to agriculture productivity. RSC has been calculated using Eq. (3). The results shown in Table 4 illustrate that RSC values range from 0.62 to 4.21 meq/l with an average of 2.4 meq/l.

Table 4: Classification of groundwater quality based on Residual Sodium Carbonate (RSC).

RSC (meq/L)	Water quality	No. of samples (%)
< 1.25	Good	3 (7%)
1.25 - 2.50	Doubtful	22 (49%)
>2.50	unsuitable	20 (44%)

These results suggest that only a small fraction (7%) of the samples exhibit good quality, whereas the remaining samples show poor water quality with 49% classified as doubtful and 44% categorized as unsuitable for irrigation use.

3.5.4 Permeability index (PI)

Soil permeability is primarily influenced by extensive use of irrigation water which comprises calcium, magnesium, sodium and bicarbonate ions. Permeability index (PI) is a valuable tool to evaluate the suitability of groundwater for irrigation purpose [44] and has been calculated using Eq. (4). The values of PI for all the groundwater samples range from 76% to 118% with an average of 95% (Table 5).

Table 5: Classification of groundwater quality based on Permeability Index (PI).

PI Classification	Water Quality	No. of Samples (%)
Class-I (>75%)	Good	45 (100%)
Class-II (75 - 25%)	Moderate	-
Class-III (<25%)	Unsuitable	-

From these results it is deduced that all the groundwater samples have good quality for irrigation use with respect to PI.

3.5.5 Kelly's ratio (KR)

Kelly's ratio calculated by Eq. (5) is used to illustrate the sodium hazard relative to the calcium and magnesium ions in irrigation water [45]. The KR values of all groundwater samples range from 0.21 to 3.47 with a mean value of 0.89. Suitability classification based on Kelly's ratio is shown in Table 6. It establishes that majority of the groundwater samples (73%) are suitable for irrigation, whilst 27% are unsuitable for irrigation use.

Table 6: Classification of groundwater quality based on Kelly's Ratio (KR).

Kelly's Ratio	Water Quality	No. of Samples (Percent)
< 1	Suitable	33 (73%)
> 1	Unsuitable	12 (27%)

3.5.6 Magnesium hazard (MH)

Magnesium hazard (MH) is used to delineate the magnesium hazard associated with plant growth [46]. A high level of magnesium in irrigation water limits water availability to the plant roots due to the adsorption of water between magnesium ion and clay particles. This rigorously affects soil infiltration characteristics and thus crop productivity. Magnesium hazard has been calculated using Eq. (6). The values of MH for groundwater samples vary from 29.7 to 93.3 with an average of 62.1. Table 7 demonstrates that only 31% of groundwater samples are suitable for irrigation; whereas, most of the samples (69%) evolved as unsuitable for irrigation use.

Table 7: Classification of groundwater quality based on magnesium hazard (MH).

Magnesium hazard (MH)	Water quality	No. of samples (%)
< 50	Suitable	14 (31%)
> 50	Unsuitable	31 (69%)

3.6 Statistical analysis

3.6.1 Principal component analysis (PCA)

Principal component analysis is a multivariate statistical tool used to analyze the variability in a dataset. PCA has been extensively used in numerous studies of surface and groundwater [47-49]. In the present study, PCA has been carried out for 10 variables (TDS, pH, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^- Ca^{2+}, Mg^{2+}, Na^+ and K^+) to extract principal factors corresponding to the different sources of variation in the data set (Fig. 7).

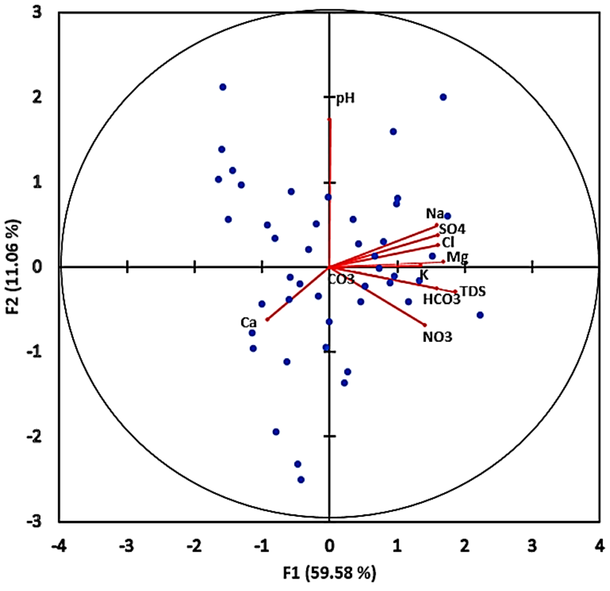

Fig. 7: Correlation plot among variables and factor loading.

Table 8: Correlations between variables and factor loading of each physicochemical parameters.

Variables	F1	F2	F3	F4
TDS	0.958	-0.153	-0.007	0.047
Ph	0.003	0.896	0.198	0.268
HCO_3^-	0.818	-0.132	-0.230	-0.029
Cl^-	0.831	0.133	0.357	0.005
SO_4^{2-}	0.830	0.193	0.276	-0.290
NO_3^-	0.728	-0.356	0.307	0.022
Ca^{2+}	-0.472	-0.322	0.714	0.297
Mg^{2+}	0.867	0.027	-0.213	0.231
Na^+	0.819	0.251	0.142	-0.325
K^+	0.703	0.009	-0.203	0.511
Variability (%)	59.579	11.055	9.149	6.096
Cumulative %	59.579	70.634	79.784	85.879

Table 9: Correlation analysis of the physiochemical parameters for groundwater samples.

Variables	TDS	pH	HCO_3	Cl	SO_4	NO_3	Ca	Mg	Na	K
TDS	1									
pH	-0.102	1								
HCO_3^-	0.818	-0.077	1							
Cl^-	0.758	0.104	0.459	1						
SO_4^{2-}	0.701	0.122	0.590	0.820	1					
NO_3^-	0.708	0.708	-0.167	0.553	0.616	1				
Ca^{2+}	-0.369	-0.056	-0.416	-0.225	-0.357	-0.089	1			
Mg^{2+}	0.825	0.079	0.737	0.642	0.602	0.627	-0.516	1		
Na^+	0.753	0.141	0.617	0.741	0.800	0.461	-0.413	0.537	1	
K^+	0.658	0.003	0.517	0.580	0.438	0.380	-0.344	0.649	0.456	1

Table 8 summarizes the PCA results and variance induced by each of the principal component. PCA rendered four principal components contributing towards the total variance of more than 86% as F1 (59.6%), F2 (11.1%), F3 (9.2%) and F4 (6.1%). PC1 explains about 60% of the total variance and constitute variables TDS, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, Mg^{2+}, Na^+ and K^+ with the highest values of absolute coefficients. This demonstrates two key aspects: firstly, groundwater is mainly originating from the chemical weathering of rock minerals and dissolution of secondary salts [50], and secondly, the positive loading of nitrate indicates influence of chemical fertilizers and improper disposal of human and animal wastes.

Whereas, PC2 explains nearly 11% of the variance, which is described by the negative loading of Ca^{2+} and HCO_3^-; and positive loadings of Na^+. This may indicate groundwater pollution by the infiltration of leachate from landfills or industrial sites [51]. Furthermore, the remaining principal factors, PC3 and PC4 account for 9% and 6% of the total variance, respectively. These PCs seem to have a random and independent correlation.

3.6.2 *Correlation analysis (CA)*

Correlation analysis frequently used in hydrological studies and numerous applications are found in the literature [52-54]. The correlation matrix (Table 9) shows that TDS and the major ions (cations and anions) have a significant positive correlation. There is significant correlation of TDS with HCO_3^- ($r^2 = 0.818$), Cl^- ($r^2 = 0.758$), SO_4^{2-} ($r^2 = 0.701$), NO_3^- ($r^2 = 0.708$), Mg^{2+} ($r^2 = 0.825$), Na^+ ($r^2 = 0.753$) and K^+ ($r^2 = 0.658$). It reveals the origin of these ions in terms of rock-water interaction and mineralization. Whereas, the nitrate ion abundance predominantly accounts for groundwater pollution is caused by anthropogenic processes.

From Table 9, it is perceptible that HCO_3^- has a good correlation with most of the variables, explaining various hydrogeochemical processes of the aquifer system such as weathering, water-rock interaction and ion exchange. However, the negative correlation of TDS with pH ($r^2 = -0.102$) and Ca^{2+} ($r^2 = -0.369$) suggested that calcite dissolution is not the prevalent phenomena related to acidic conditions of groundwater. All other variables including Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} bear a good correlation among each other.

4. Conclusions

Sustainability of groundwater resources is imperative to meet the escalating water requirement of the growing population for higher agricultural yield and drinking purposes. Therefore, concerning the present situation of water scarcity, especially in semi-arid areas, this study delineates vital information about hydrogeochemical characteristics and groundwater quality for drinking and irrigation uses. The analytical data has been processed to extract useful information, using multiple graphical software and multivariate statistical methods.

The results demonstrate that groundwater quality for drinking as well as irrigation purposes is generally well within the permissible limits of WHO and irrigation suitability guidelines; however, a few irrigation suitability parameters such as RSC and MH exceed the permissible limits, indicating input from either domestic sewage or agricultural fertilizers. Moreover, it is deduced that Ca-Mg-HCO_3 is the most abundant hydrochemical facies in groundwater and silicate weathering is the fundamental process controlling the hydrogeochemical formation of the aquifer system in the study area. On the other hand dolomite dissolution is recognized as the leading mineral phase during water-rock interaction. Principal component analysis unveiled correlation among different variables and identified the key processes and sources of hydrogeochemical origin and groundwater pollution. PCA not only elucidates chemical weathering of rocks as primary phenomena controlling the mineral dissolution but pronounces that the intervention of anthropogenic sources is also an important factor for groundwater pollution.

Understanding of groundwater origin, mineralization processes and water quality are the characteristic features of hydrogeological investigations. This study provides a comprehensive knowledge of the hydrogeochemical characteristics and groundwater quality of the study area, which will enable the decision-makers and water resource managers to develop a better management strategy to cope with the ever-increasing water demands by appropriate allocation of groundwater resources for domestic and agricultural purposes.

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