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Multidimensional Assessment of Groundwater in Reyhanlı (Hatay, Türkiye): Hydrogeochemistry, Irrigation Suitability and Health Risk Assessment

Reyhanlı'da (Hatay, Türkiye) Yeraltı Suyunun Çok Boyutlu Değerlendirmesi: Hidrojeokimya, Sulama Uygunluğu ve Sağlık Riski Değerlendirmesi

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Abstract

Groundwater is a valuable resource for drinking, irrigation, and industrial applications in arid and semi-arid regions. Groundwater quality is an important issue that should be monitored for both human consumption and agricultural irrigation. However, groundwater quality, suitability of groundwater for irrigation, and its risk assessment for human health in the Reyhanlı district of Hatay province, located in southern Türkiye, have not been sufficiently investigated. In this study, for the first time, the chemical composition of groundwater in the Reyhanlı district, the factors/mechanisms controlling its composition, its suitability for irrigation, as well as the non-carcinogenic health risks of metal(loid)s in the groundwater for adults and children were determined. The pH, electrical conductivity (EC), total dissolved solids (TDS) values, as well as concentrations of major ions, boron, and various metal(loid)s (As, Al, Fe, Mn, Ni, Cr, Cu, Co, Cd, Pb, Zn) in groundwater were determined. Piper diagram, Gibbs diagram, and chloroalkaline indices were used to determine the hydrochemical facies of groundwater, the main mechanisms controlling groundwater chemistry, and the direction of the ion exchange process, respectively. The suitability of groundwater for irrigation was investigated by calculating SAR, Na%, SSP, RSC, MH, PI, PS, and KR indices. In addition, the suitability of groundwater for irrigation was assessed using the United States Salinity Laboratory (USSL) diagram and the Wilcox diagram. According to the Weighted Arithmetic Water Quality Index (WAWQI), all groundwater was classified as "excellent". The levels of metal(loid)s in all groundwater samples comply with the WHO guideline values for drinking water. The results of the health risk assessment have shown that the hazard quotients and hazard index are less than 1 for both adults and children, indicating that the groundwater does not pose a health risk.

Keywords: *Groundwater, Irrigation, Drinking Water, Water Quality Index, Hazard Index, Health Risk*

Öz

Yeraltı suyu kurak ve yarı kurak bölgelerde içme, sulama ve endüstriyel uygulamalar için değerli bir kaynaktır. Yeraltı suyu kalitesi, hem insan tüketimi hem de tarımsal sulama için izlenmesi gereken önemli bir konudur. Ancak, Türkiye'nin güneyinde yer alan Hatay ilinin Reyhanlı ilçesinde yeraltı suyu kalitesi, yeraltı suyunun sulama için uygunluğu ve insan sağlığı için risk değerlendirmesi yeterince araştırılmamıştır. Bu çalışmada, ilk kez Reyhanlı ilçesindeki yeraltı sularının kimyasal bileşimi, kimyasal bileşimini kontrol eden faktörler/mekanizmalar, sulama için uygunluğunun yanı sıra yeraltı suyundaki metal(oid)lerin yetişkinler ve çocuklar üzerindeki kanserojen olmayan sağlık riski belirlenmiştir. Yeraltı sularında pH, elektriksel iletkenlik (EC), toplam çözünmüş katı madde (TDS) değerlerinin yanı sıra majör iyonlar, bor ve çeşitli metal(oid)lerin (As, Al, Fe, Mn, Ni, Cr, Cu, Co, Cd, Pb, Zn) konsantrasyonları belirlenmiştir. Piper diyagramı, Gibbs diyagramı ve kloroalkali indeksleri sırasıyla yeraltı suyunun hidrokimyasal fasiyeslerini, yeraltı suyu kimyasını kontrol eden ana mekanizmaları ve iyon değişim sürecinin yönünü belirlemek için kullanılmıştır. Yeraltı suyunun sulama için uygunluğu SAR, Na%, SSP, RSC, MH, PI, PS ve KR indisleri hesaplanarak araştırılmıştır. Ayrıca, yeraltı suyunun sulama için uygunluğu Amerika Birleşik Devletleri Tuzluluk Laboratuvarı diyagramı ve Wilcox diyagramı kullanılarak değerlendirilmiştir. Ağırlıklı aritmetik su kalitesi indeksine (WAWQI) göre, tüm yeraltı suları "mükemmel" olarak sınıflandırılmıştır. Tüm yeraltı suyu örneklerindeki metal(oid)lerin seviyeleri WHO'nun içme suyu kılavuz değerleriyle uyumludur. Sağlık risk değerlendirmesinin sonuçları, hem yetişkinler hem de çocuklar için tehlike katsayılarının ve tehlike indeksinin 1'den düşük olduğunu göstermiştir; bu da yeraltı suyunun sağlık riski oluşturmadığını göstermektedir.

Anahtar Kelimeler: *Yeraltı Suyu, Sulama, Içme Suyu, Su Kalitesi Indeksi, Tehlike Indeksi, Sağlık Riski*

1. Introduction

Water scarcity and poor water quality are significant concerns on a global scale. To address the water demand of the population, governments are undertaking initiatives to obtain additional high-quality water resources [1]. In arid and semi-arid regions, where surface water availability is limited and precipitation is scarce, groundwater emerges as a valuable resource for various uses, including agricultural irrigation, domestic consumption, and industrial applications [2,3]. Moreover, in regions with high population density and limited access to surface water, groundwater is emerging as a crucial resource to facilitate regional development [4]. Worldwide, 65% of available groundwater is used for drinking, 20% for irrigation, and 15% for industrial applications [5]. Groundwater provides the drinking water needs of one-third of the world's population [6]. Globally, freshwater is mostly used for irrigation, and irrigated agriculture accounts for 85-90% of global water consumption [7]. It is estimated that agricultural production and water withdrawals to

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feed the planet will increase by 50% and 15%, respectively by 2050 [8].

Groundwater quality depends on many factors such as hydrogeochemical processes, precipitation, the characteristics of recharging water, and anthropogenic activities [9]. The use of low-quality water causes diseases, negative effects on the ecosystem, and economic losses [10]. Moreover, the use of low-quality groundwater for irrigation causes a decrease in soil fertility and crop productivity [11].

The sustainability and assessment of groundwater quality are areas of growing importance worldwide [12]. Investigating the composition of groundwater and its suitability for different purposes provides a good reference for groundwater management [13]. In different parts of the world, studies have been carried out to analyze groundwater composition [14–19], and assess the suitability of groundwater for use [14,18]. Despite the increasing importance of groundwater monitoring in semi-arid agricultural regions, comprehensive studies addressing both groundwater quality and health risk assessment remain limited in many parts of the world. The hydrochemistry and human health risk of groundwater in the Reyhanlı district of Hatay province, located on the Turkish-Syrian border, have not been previously investigated. This study provides, for the first time, a comprehensive assessment of groundwater in Reyhanlı, Hatay, including factors affecting its composition, suitability for irrigation, and assessment of potential non-carcinogenic human health risk.

2. Materials and Methods

2.1. Groundwater sampling area

Reyhanlı is a district of Hatay province in Türkiye, located on the border between Türkiye and Syria. Drinking water needs in the Reyhanlı district of Hatay are met by more than 20 deep wells. In the Reyhanlı district, 330 L/s and 450 L/s of water are obtained from existing wells in the summer and winter seasons, respectively. However, since the water obtained from the existing wells is not sufficient for the increasing population, four more deep wells were drilled in the Gazimürsel region to meet the increasing water demand (GW1, GW2, GW3, and GW4). Figure 1 shows the Reyhanlı district of Hatay and the sampling area where groundwater samples were collected.

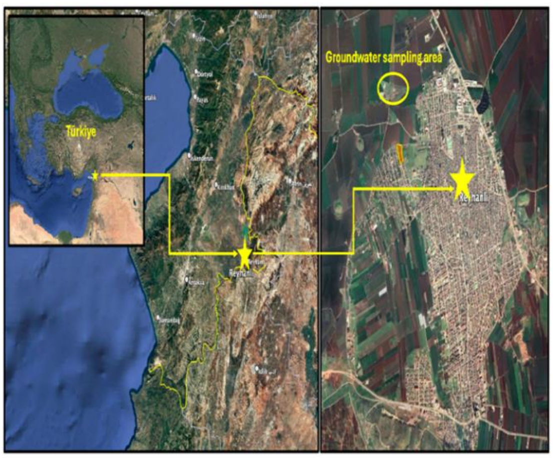

Figure 1. Groundwater sampling site in the Reyhanlı district.

In the area where groundwater samples were collected, there is an organic-rich surface soil layer with a thickness of 0–30 cm. Up to a depth of 20 meters, soil units belonging to lake bottom deposits are present, consisting of gray-brown, naturally moist, very stiff sandy clay and silty sand mixtures. The age of the formation is Quaternary. Additionally, in nearby areas close to the groundwater sampling site, the Langhian–Serravallian-aged Tepehan Formation is present, characterized by a lithology of sandstone, clayey limestone, claystone, and marls.

2.2. Groundwater analysis methods

Groundwater quality data used in this study, including sampling and laboratory analyses, were obtained from the General Directorate of Water and Sewerage Administration of the Hatay Metropolitan Municipality. Groundwater samples from all wells were collected at the end of August 2023. Groundwater sampling was conducted from wells with a depth of 80 m. The collected groundwater samples were analyzed for pH, EC, TDS, sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sulfate (SO_4^-), nitrate (NO_3^-) bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), chloride (Cl^-), boron (B), aluminum (Al), arsenic (As), iron (Fe), manganese (Mn), nickel (Ni), chromium (Cr), copper (Cu), cobalt (Co), cadmium (Cd), lead (Pb) and zinc (Zn) analyses were performed. TS EN ISO 10523 and TS 9748 EN 27888 methods were used for pH and EC analysis of groundwater samples, respectively. Na^+, K^+, Ca^{2+}, and Mg^{2+} concentrations in groundwater samples were determined by the TS EN ISO 14911 method. HCO_3^- and CO_3^{2-} analyses were performed using the TS 3790 EN ISO 9963-1 method. SO_4^{2-}, Cl^-, and NO_3^- concentrations of groundwater samples were determined by the TS EN ISO 10304-1 method. B, Al, As, Fe, Mn, Ni, Cr, Cu, Co, Cd, Pb, and Zn analyses were performed by the TS EN ISO 17294-2 method.

2.3. Irrigation water quality indices

Sodium adsorption ratio (SAR), sodium percentage (Na%), soluble sodium percentage (SSP), residual sodium carbonate (RSC), magnesium hazard (MH), Kelly's ratio (KR), permeability index (PI) and potential salinity (PS) values were calculated using Equations 1–8 to determine the suitability of groundwater samples for irrigation [20,21].

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \tag{1}$$

$$Na\% = \frac{Na^+ + K^+}{Ca^{2+}+Mg^{2+}+Na^+ + K^+} x\ 100 \tag{2}$$

$$SSP = \frac{Na^+}{Ca^{2+}+Mg^{2+}+Na^+} x\ 100 \tag{3}$$

$$RSC = \left(HCO_3{}^- + CO_3{}^{2-}\right) - \left(Ca^{2+} + Mg^{2+}\right) \tag{4}$$

$$MH = \frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}} x\ 100 \tag{5}$$

$$KR = \frac{Na^+}{Ca^{2+}+Mg^{2+}} \tag{6}$$

$$PI = \frac{Na^+ + \sqrt{HCO_3{}^-}}{Na^+ + Ca^{2+} + Mg^{2+}} \tag{7}$$

$$PS = Cl^- + \frac{1}{2} SO_4{}^{2-} \tag{8}$$

Anion and cation concentrations in Equations 1–8 are in meq/L.

2.4. Calculation of corrosivity ratio

Corrosivity ratio (CR) values for groundwater were calculated using Equation 9 to determine the corrosion tendency of groundwater on metallic pipes [22].

$$CR = \frac{\frac{Cl^-}{35.5} + \frac{SO_4{}^{2-}}{48}}{\frac{(CO_3{}^{2-} + HCO_3{}^-)}{50}} \tag{9}$$

2.5. Calculation of chloroalkaline indices (CAIs)

Chloroalkaline indices (CAIs) of groundwater were calculated using Equations 10 and 11 [23].

$$CAI-1=\frac{Cl^{-}-(Na^{+}+K^{+})}{Cl-} \quad (10)$$

$$CAI-2=\frac{Cl^{-}-(Na^{+}+K^{+})}{HCO_3{}^{-}+CO_3{}^{2-}+SO_4{}^{2-}+NO_3{}^{-}} \quad (11)$$

2.6. Determination of the weighted arithmetic water quality index (WAWQI)

The water quality index (WQI) value of groundwater was calculated by the weighted arithmetic water quality index (WAWQI) method considering pH, EC, TDS, major anions and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$) as well as metal(loids) parameters (e.g. Al, As, Cd, Cr, Cu, Pb, Zn, Fe, Mn, Ni and B). The WAWQI is one of the most widely used methods for assessing the WQI of water. The WAWQI method is a simple yet effective approach that incorporates physico-chemical water quality data into a mathematical formula, enabling a straightforward assessment of overall water quality [24]. The WAWQI method is flexible and can be applied using different types and numbers of water quality parameters. Additionally, it yields a single numerical value based on a set of water quality parameters for a given water sample, which serves as an indicator of general water quality. This allows for the simplification and interpretation of complex water quality datasets using easily understandable categories such as excellent, very good, good, poor, and unsuitable [25]. Moreover, the WAWQI approach assigns weights to individual water quality parameters, thereby allowing for the evaluation of each parameter's specific contribution to the overall water quality. The WAWQI was calculated using Equations 12–15 [26–28]. In the first step of calculating the WAWQI of groundwater samples, the unit weight (W_n) of the parameters in the groundwater was calculated.

$$W_n=\frac{K}{S_n} \quad (12)$$

Where K and S_n are the proportionality constant and the permissible value (standard value) for the nth parameter, respectively.

The K value was determined using the following equation:

$$K=\frac{1}{\sum_{i=1}^{n}\frac{1}{S_n}} \quad (13)$$

The quality rating (qn) of the nth parameter in the groundwater samples was calculated using Equation 14.

$$qn=\left(\frac{V_n-V_i}{V_s-V_i}\right)x\ 100 \quad (14)$$

Where V_n is the nth parameter measured in groundwater samples, V_i is the ideal value for the nth parameter, and V_s is the standard value for the nth parameter. V_i is 7 for the pH parameter and 0 for all other parameters (EC, TDS, anions, and cations) in groundwater [29]. Table 1 shows standard values, ideal values, and unit weights of parameters used in the WAWQI calculation.

In the last step, the WAWQI values of the groundwater samples were determined using Equation 15.

$$WAWQI=\frac{\sum_{i=1}^{n}W_n x\ q_n}{\sum_{i=1}^{n}Wn} \quad (15)$$

Table 1. Standard values, ideal values, and unit weights of parameters used in the WAWQI calculation.

Parameter	S_n	$1/S_n$	$W_n=K/S_n$	V_i
pH	8.5	0.118	0.000196	7
TDS (mg/L)	500	0.002	0.000003	0
Na (mg/L)	200	0.005	0.000008	0
K (mg/L)	10	0.100	0.000167	0
Ca (mg/L)	75	0.013	0.000022	0
Mg (mg/L)	30	0.033	0.000056	0
Cl (mg/L)	250	0.004	0.000007	0
SO_4 (mg/L)	250	0.004	0.000007	0
NO_3 (mg/l)	50	0.020	0.000033	0
Al (mg/L)	0.2	5	0.008346	0
As (mg/L)	0.01	100	0.166921	0
Cd (mg/L)	0.003	333.333	0.556403	0
Cr (mg/l)	0.05	20	0.033384	0
Cu (mg/L)	2	0.500	0.000835	0
Pb (mg/L)	0.01	100	0.166921	0
Zn (mg/L)	3	0.333	0.000556	0
Fe (mg/L)	0.3	3.333	0.005564	0
Mn (mg/L)	0.05	20	0.033384	0
Ni (mg/L)	0.07	14.286	0.023846	0
B (mg/L)	0.5	2	0.003338	0

2.7. Calculation of hazard quotient (HQ) and hazard index (HI)

Assessing the human health risk of contaminants in water is useful for predicting potential adverse health effects for the population that will consume this water and for developing strategies to provide safe drinking water to the population [30]. To determine the possible negative impact on human health by ingestion of metals-contaminated groundwater, chronic daily intake (CDI) (mg/kg.day) was calculated for both adults and children using Equation 16 [31].

$$CDI(ingestion)=\frac{C\ x\ IR\ x\ ED\ x\ EF}{BW\ x\ AT} \quad (16)$$

Where C is the metal concentration in groundwater (mg/L), IR is the ingestion rate (L/day), ED is the exposure duration (years), EF is the exposure frequency (days/year), BW is the body weight (kg), and AT is the average time (AT = ED × 365) (days). In the calculation of the CDI value for adults (CDI_{adult}), IR, ED, EF, BW, and AT values were assumed to be 2 L/day, 30 years, 350 days/year, 70 kg, and 10950 days, respectively. In the calculation of the CDI value for children ($CDI_{children}$), IR, ED, EF, BW, and AT values were assumed to be 1 L/day, 6 years, 350 days/year, 15 kg, and 2190 days, respectively.

After determining the CDI values, Equation 17 was used to determine the HQ (dimensionless) for non-carcinogenic risk [32].

$$HQ=\frac{CDI(ingestion)}{RfD(ingestion)} \quad (17)$$

Where RfD is the reference dose of the metal by oral exposure. In the calculation of HQ values for both adults and children (HQ_{adults} and $HQ_{children}$), RfD values for Fe, Mn, Ni, Cr, Cd, Pb, Zn, Al, As, Cu and Co were 0.7, 0.14, 0.02, 0.003, 0.0005, 0.0035, 0.3, 1, 0.0003, 0.04 and 0.0003 mg/kg.day, respectively [33,34].

If the HQ value is greater than 1 (>1), the risk of adverse non-carcinogenic health effects is unacceptable. If the HQ value is less than 1 (<1), the risk is acceptable. An increasing HQ value indicates an increasing risk.

In the final step, the HQ value for each metal is summed to calculate the Hazard Index (HI), which indicates the overall risk (Equation 18) [32].

$$HI = \sum_{i=1}^{n}(HQ)n \quad (18)$$

Where n is the number of metals considered in the groundwater sample. If the HI value is less than 1 (<1), the overall adverse non-carcinogenic effect of exposure by ingestion is acceptable. If the HI value is greater than 1 (>1), the risk is not acceptable.

3. Results and Discussion

3.1. Chemical characteristics of groundwater

Figure 2 shows the concentration of cations and anions in the groundwater samples. The mean concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+} in the groundwater samples were 174.3±5.58–479.16±15.33, 5.84±0.29–7.72±0.38, 25.89±1.63–91.22±5.75, and 34.86±0.7–55.07±1.1 respectively. The mean CO_3^{2-} concentration in all groundwater samples was 0 mg/L and the mean HCO_3^- concentration varied between 243.41–247.44 mg/L. The mean Cl^-, SO_4^{2-} and NO_3^- concentrations varied between 239.69±11.03–756.29±34.79, 48.52±1.36–116.58±3.26 and 20.4±4.63–61±13.85 mg/L, respectively. The cations with the highest and lowest concentrations in all groundwater were Na^+ and K^+, respectively. Cation concentrations in the GW1, GW2, and GW3 samples followed the decreasing order of $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, whereas in the GW4 sample, the sequence was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. In the GW1, GW2, and GW3 samples, anion concentrations were ordered as $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. In contrast, the GW4 sample exhibited a different anionic sequence: $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$.

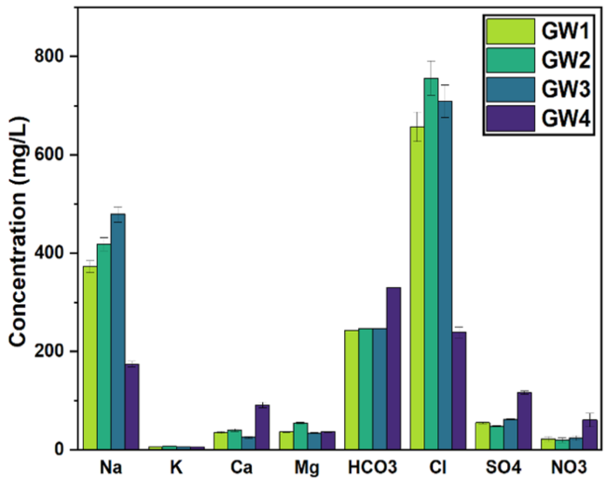

Figure 2. The concentration of cations and anions in groundwater samples.

The Schoeller diagram is a semi-logarithmic diagram used to show the concentration of major ions expressed in meq/L and to compare the concentration of major ions in multiple water analyses [35]. Figure 3 shows the Schoeller diagram of groundwater samples. According to the Schoeller diagram of the groundwater samples, the dominant cation and anion species were Na^+ and Cl^-, respectively. The Piper diagram can be used to determine the type/hydrochemical facies of groundwater based on the major ions in the groundwater [36]. Figure 4 shows the type of groundwater according to the Piper diagram. GW1, GW2, and GW3 samples were "Na–Cl water type" while GW4 was closer to "mixed water type". The predominance of Na–Cl type groundwater in the region can be attributed to the synergistic influence of geological, climatic, and anthropogenic factors, including the natural geological formations of the Reyhanlı district, semi-arid climate conditions, high evaporation rates, excessive groundwater extraction, and the intensive application of fertilizers and pesticides in agricultural activities [37].

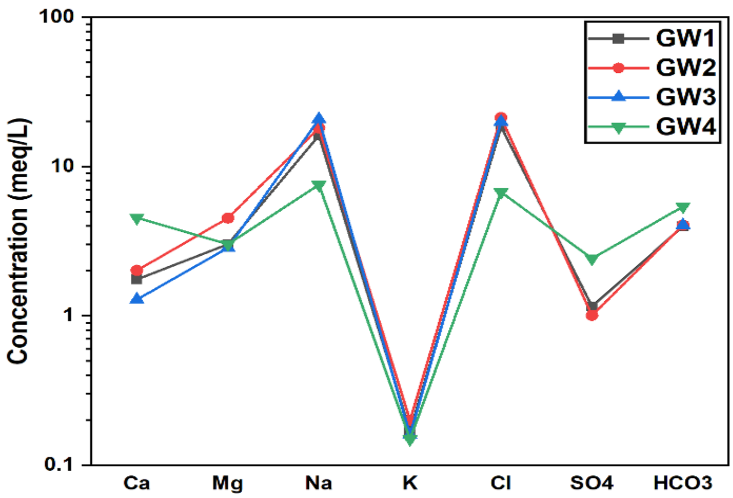

Figure 3. Schoeller diagram of groundwater samples.

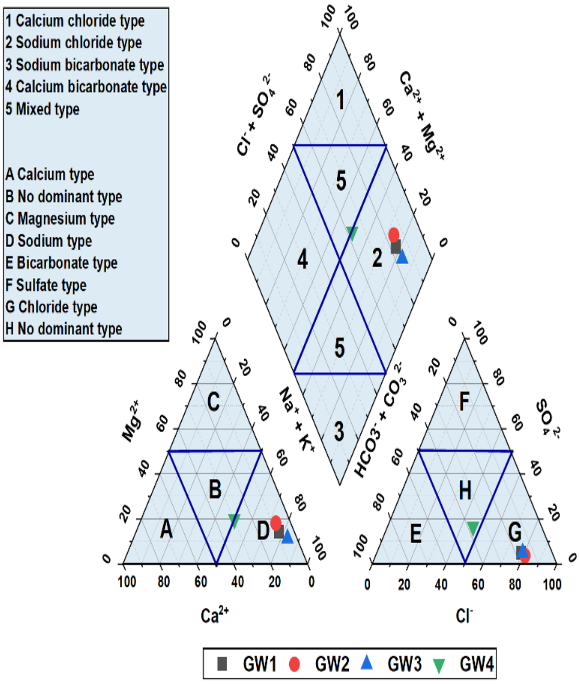

Figure 4. Piper diagram of groundwater samples.

3.2. Factors affecting groundwater chemistry

Gibbs diagram is widely used to determine the main factor affecting the chemistry of groundwater. In the Gibbs diagram, the ratios of $Na^+/(Na^++Ca^{2+})$ versus TDS and $Cl^-/(Cl^-+HCO_3^-)$ versus TDS can be used to determine the mechanisms affecting the chemistry of groundwater. The Gibbs diagram is divided into three zones: rock dominance zone, precipitation dominance zone, and evaporation dominance zone. Low $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ ratios and moderate TDS values indicate that rock weathering is the dominant factor in groundwater chemistry (Middle part of the Gibbs diagram) [38]. High $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ ratios and high TDS levels indicate that evaporation is the dominant factor in groundwater chemistry (Upper right part of the Gibbs diagram). Evaporation of groundwater increases the TDS value of water and the concentration of major ions [39]. The precipitation dominance zone, which indicates that atmospheric precipitation is the main factor controlling the chemistry of groundwater in the Gibbs diagram, includes the region with lower TDS values but higher $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^-+HCO_3^-)$ ratios (Lower right part of the Gibbs diagram). Figure 5 shows the Gibbs diagram of groundwater samples. The shift of groundwater samples from the rock dominance zone in the middle of the diagram to the upper part of the diagram showed that the hydrochemistry of groundwater is mainly controlled by rock erosion and evaporation factors. The evaporation factor can increase salinity and TDS by elevating the Na^+ and Cl^- concentration of groundwater [40].

As groundwater moves through the aquifer, its chemical composition is altered by various mineral interactions [41]. Ion exchange and sorption mechanisms are effective in the concentration and migration of ions in groundwater [42]. Ion exchange between water and rocks plays an important role in changing the ion concentration of groundwater. Schoeller developed CAI–1 and CAI–2 to evaluate these interactions [43]. If CAIs are positive, this indicates that Na^+ and K^+ in groundwater are exchanged with Mg^{2+} and Ca^{2+} in rock (aquifer medium) (reverse ion exchange reaction). As a result, Ca^{2+} and Mg^{2+} in groundwater increase [41]. On the other hand, if CAIs are negative, this indicates that Ca^{2+} and Mg^{2+} in groundwater are exchanged with Na^+ in the rock, and the Na^+ concentration in groundwater increases (direct ion exchange reaction) [44]. CAI–1 and CAI–2 were both positive for GW1 and GW2 but negative for GW3 and GW4, indicating that reverse ion exchange reaction was the main mechanism in GW1 and GW2 and ion exchange reaction in GW3 and GW4 (Figure 6).

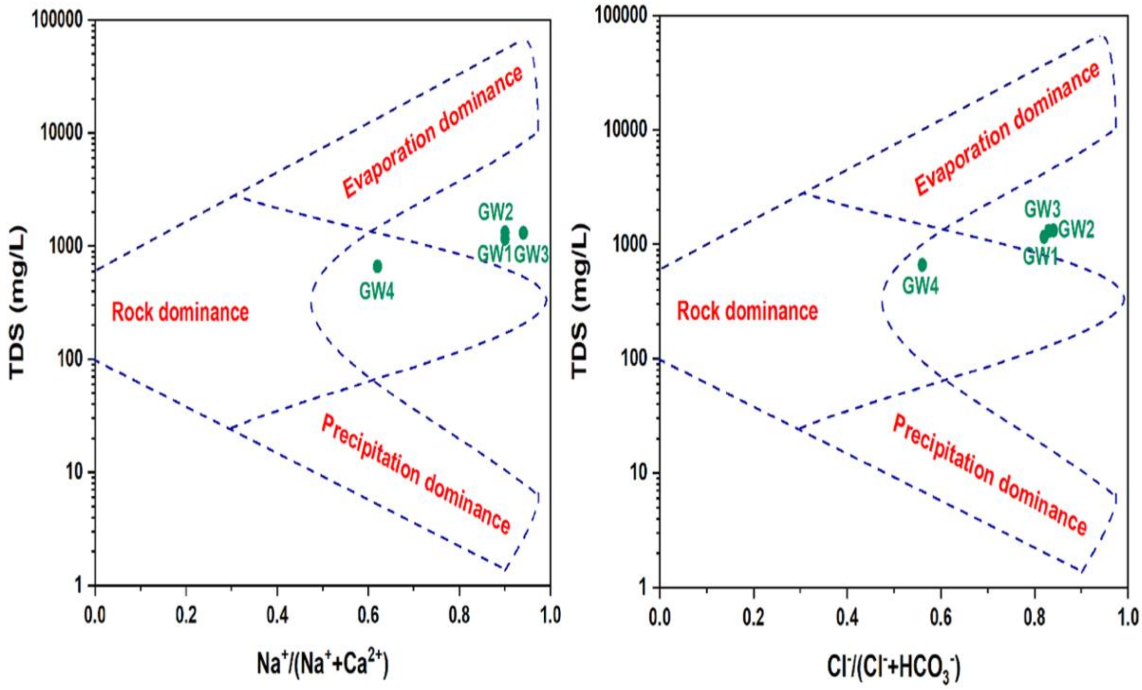

Figure 5. Gibbs diagram of groundwater samples.

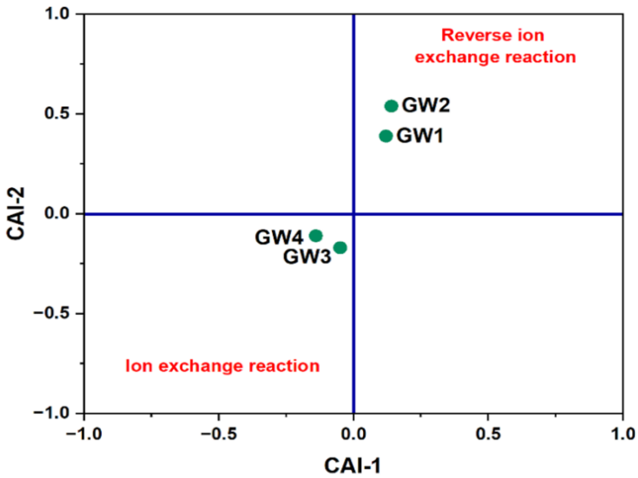

Figure 6. CAIs of groundwater samples.

3.3. Assessment of the suitability of groundwater for irrigation

3.3.1. pH

The pH of water is an important factor affecting soil microbiology, the plant root system, and the cation exchange process between soil and plant. [45,46]. The pH of the water can also affect the pH of the soil, corrosion of irrigation equipment, pesticide efficacy, and nutrient availability [47]. The optimum pH for the use of groundwater as irrigation water is recommended to be in the range of 6.5–8.5 [48]. The pH values of GW1, GW2, GW3 and GW4 samples were 7.94±0.03, 8.05±0.03, 8.16±0.03 and 7.46±0.03, respectively. All groundwater samples were slightly alkaline, and all groundwater samples were in the optimum pH range for irrigation.

3.3.2. Electrical conductivity (EC) and total dissolved solids (TDS) values

EC is a widely used parameter in groundwater monitoring studies because it indicates the presence of dissolved ions, indicating natural changes or pollution of water [49]. The EC value of groundwater varied between 1461±10.3 and 2,640±10.3 µS/cm (Figure 7). According to the classification of saline water, waters with EC values <700 µS/cm are considered suitable for both drinking and irrigation purposes. Waters with EC values between 700 and 2,000 µS/cm are categorized as irrigation water, while those with EC values ranging from 2,000 to 10,000 µS/cm are categorized as primary drainage water or groundwater (Table 2). Considering the EC value, groundwater was in the "irrigation water" and "primary drainage water and groundwater" water types and in the "slightly saline" and "moderately saline" water classes (Table 2). According to EC values, GW4 belongs to class C3 (high salinity water) since its EC value is between 750–2,250 µS/cm. GW1, GW2, and GW3 belong to class C4 (very high salinity water) since their EC values are >2,250 µS/cm. GW4 is not suitable for the irrigation of crops without good salt tolerance and in soils with limited drainage. The very high EC value of GW1, GW2, and GW3 indicates that these waters are not suitable for irrigation under normal conditions. The use of water with high salinity in irrigation can lead to the salinization of agricultural land, and increase the osmotic pressure of the soil solution, which can result in the inability of plants to take up water and nutrients through their roots and reduce yield potential [50,51]. The EC threshold value of irrigation water varies according to crop type, and water with an EC lower than 700 µS/cm is safe for most crops. Crops such as beans, peppers, carrots, onions, lettuce, spinach, cucumbers, tomatoes, and eggplants are grown in Hatay, Reyhanlı [52]. For instance, considering the EC value of irrigation water, crops such as beans, carrots, onions, and spinach are in the "sensitive" group, while crops such as tomatoes, peppers, eggplants, and lettuce are in the "moderately sensitive" group [53].

TDS is a term describing inorganic salts and small amounts of organic matter dissolved in water [54]. The TDS value of groundwater samples varied between 664.49±5–1,326.68±10.5 mg/L (Figure 7). As the EC values of groundwater samples increased, the TDS values also increased, indicating a positive relationship between the two parameters. The TDS value of brackish water is generally in the range of 1,000–10,000 mg/L, and this type of water is in the range of freshwater (TDS: <1,000 mg/L) and saline water (TDS: >10,000 mg/L) [55]. In the study, GW4, which has a lower TDS value (664.49 mg/L) compared to other groundwater, was characterized as "freshwater". On the other hand, the TDS values of GW1, GW2, and GW3 were in the range of 1,000–10,000 mg/L (1,164.58–1,326.68 mg/L), indicating that these waters were classified as "brackish water". Since the TDS values of the groundwater were lower than 3,000 mg/L, the TDS values of the waters were suitable for the use of the waters for irrigation [56].

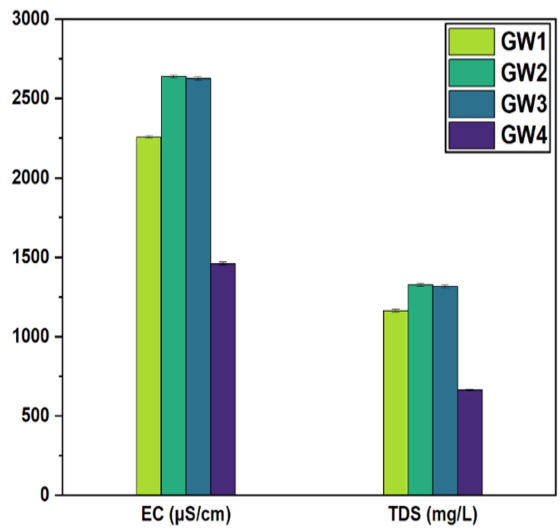

Figure 7. EC and TDS values of groundwater samples.

3.3.3. Sodium adsorption ratio (SAR)

The sodium hazard posed by irrigation water is assessed by SAR. The use of water with high SAR in agricultural irrigation not only negatively affects the soil structure but also changes the permeability of the soil. The application of irrigation water with high SAR values to the soil leads to the replacement of Mg^{2+} and Ca^{2+} by Na^{+} and changes in soil permeability. Water with a SAR value <10 is suitable for agricultural irrigation. Except for GW4, the SAR values of the groundwater analyzed (10.06–14.45) were between 10–18, so these waters were classified as medium-sodium water (S2). Since the SAR value of GW4 was <10 (3.08), the SAR value of this water was quite suitable for use in agricultural irrigation. According to the United States Salinity Laboratory (USSL) diagram, GW1 and GW2 were classified as C4S3, GW3 as C4S4, and GW4 as C3S1 (Figure 8).

Table 2. Classification of irrigation water according to salinity, EC values, and SAR values.

	EC (µS/cm)	Class	Water type
Classification of saline waters [57]	<700	Non-saline	Drinking and irrigation water
	700–2,000	Slightly saline	Irrigation water
	2,000–10,000	Moderately saline	Primary drainage water and groundwater
	10,000–25,000	Highly saline	Secondary drainage water and groundwater
	25,000–45,000	Very highly saline	Very saline groundwater
	>45,000	Brine	Seawater
	EC (µS/cm)	**Class**	**Suitability for irrigation**
Classification of irrigation water according to EC value [58,59]	<250	Low salinity water (C1)	Suitable for irrigation of most crops on most soils. Permissible under normal irrigation practices (except in soils with extremely low permeability).
	250–750	Medium salinity water (C2)	This type of water is usable with moderate seepage. Plants with moderate salt tolerance can be grown without special treatments for salinity control in most cases.
	750–2,250	High salinity water (C3)	Not suitable for soils with restricted drainage. Plants with good salt tolerance should be selected.
	>2,250	Very high salinity water (C4)	Not suitable for irrigation under normal conditions. The soils must be permeable. Drainage must be adequate. Plants that are very salt tolerant should be selected.
	SAR	**Class**	**Suitability for irrigation**
Classification of water according to SAR value [59,60]	<10	Low sodium water (S1)	There is little danger of developing harmful exchangeable sodium levels. Suitable for irrigation on almost all soils. (Excellent for irrigation)
	10–18	Medium sodium water (S2)	Sodium hazard occurs in fine-textured soils with high cation exchange capacity. Suitable for use on coarse-textured or organic soils with good permeability. (Good for irrigation)
	18–26	High sodium water (S3)	Produces exchangeable sodium at harmful levels in most soils.

		Requires specialized soil management (good drainage, high leaching, addition of organic matter). (Permissible for irrigation)
>26	Very high sodium water (S4)	Generally unsatisfactory for irrigation. (Unsuitable for irrigation)

3.3.4. Sodium percentage (Na%) and soluble sodium percentage (SSP)

The particles of clay and soil are mostly surrounded by Ca^{2+} ions, so they are held tightly together even in water. On the other hand, when clay particles are mostly surrounded by Na^{+} ions, the bonding of the particles is weaker, and this causes the particles to disperse when the soil is wet [61]. High sodium in irrigation water has undesirable effects on soil structure and permeability. Characteristics of sodic soils include low infiltration, poor soil structure, and poor aeration [62]. If the Na^{+} concentration in irrigation water is high, the capacity of water to move through the soil is reduced [63]. The %Na values of GW1, GW2, GW3, and GW4 were 77.40, 73.75, 83.46, and 50.47, respectively. Based on the percentage of sodium (%Na), water is classified as excellent (<20), good (20–40), permissible (40–60), doubtful (60–80), and unsuitable (>80) for irrigation purposes [64]. According to %Na values, GW1 and GW2 were “doubtful”, GW3 was “unsuitable”, and GW4 was “permissible for irrigation use”. According to the Wilcox diagram, GW1, GW2, and GW3 were classified as “doubtful to unsuitable” and GW4 as “permissible to doubtful” (Figure 9).

SSP values of GW1, GW2, GW3, and GW4 were 77.21, 73.54, 83.36, and 49.98, respectively. An SSP value of >50 indicates that the water is not suitable for irrigation use, and a value of <50 indicates that it is suitable. Among the groundwater analyzed, GW4 was suitable for use in agricultural irrigation since the SSP value of GW4 was <50.

3.3.5. Residual sodium carbonate (RSC)

The excess of CO_3^{2-} and HCO_3^{-} causes precipitation of Ca^{2+} and Mg^{2+} in the soil. This activates Na^{+} in the soil and leads to an increase of Na^{+} in the exchange complex with a loss of Ca^{2+} and Mg^{2+} [65,66]. According to the RSC range, sodium hazard is divided into three classes: good (<1.25), doubtful (1.25-2.5), and unsuitable (>2.5) [67]. Water with an RSC value greater than 2.5 is not suitable for use in agricultural irrigation. In this study, RSC values of GW1, GW2, GW3, and GW4 were -0.80, -2.49, -0.1, and -2.17 meq/L, respectively. In terms of RSC values, it was determined that all groundwater can be used in agricultural irrigation without creating an alkali hazard.

3.3.6. Magnesium hazard (MH)

Waters are suitable for agricultural irrigation while waters with MH values >50% are not suitable for agricultural irrigation [68]. The MH values of GW1, GW2, and GW3 were in the range of 63.30%–68.94%, indicating that these three groundwater bodies were not suitable for agricultural irrigation in terms of MH. However, GW4 was suitable for agricultural irrigation as its MH value (39.98%) was <50%.

3.3.7. Kelly’s ratio (KR)

KR is a parameter introduced to assess the suitability of water for irrigation [69]. The calculation of KR is based on the concentration of Na^{+}, Ca^{2+}, and Mg^{2+} in the water. A KR value greater than 1 indicates a high amount of Na+ in the water and indicates that the water is not suitable for irrigation. A KR value <1 indicates that the water is suitable for irrigation. In this study, while the KR value of GW4 was 1, the KR values of GW1, GW2, and GW3 varied between 2.78–5.01. The KR values calculated for groundwater indicated that the GC value of GW4 was suitable for irrigation, while the other groundwater was not suitable.

3.3.8. Permeability index (PI) and potential salinity (PS)

The PI formulation developed to assess the effect of the chemical composition of irrigation water on soil permeability is widely used [70]. Soil permeability is affected by Na^{+}, Ca^{2+}, Mg^{2+}, and HCO_3^{-} content [14]. By considering the Na^{+}, Ca^{2+}, Mg^{2+}, and HCO_3^{-} content in the irrigation water in the PI formulation, it can be determined whether there is a risk of reducing the permeability of the soil. In the PI diagram, waters included in Class I (suitable) and Class II (good) are suitable for irrigation, while waters included in Class III (unsuitable) are not suitable for irrigation [70,71]. According to the PI diagram, GW1 and GW3 were included in Class II, and GW2 and GW4 were included in Class I (Figure 10). All groundwater was of “suitable” and “good” quality in terms of PI.

Salts can accumulate in the soil and increase soil salinity [72]. Waters with PS values <3 meq/L are suitable for agricultural irrigation [73]. Since the PS value of all groundwater is in the range of 7.97–21.84 meq/L, groundwater is not suitable for irrigation in terms of PS.

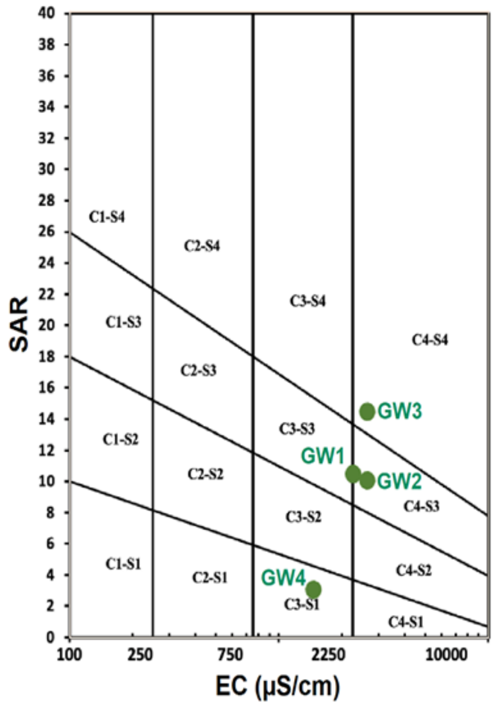

Figure 8. USSL diagram showing groundwater quality for irrigation.

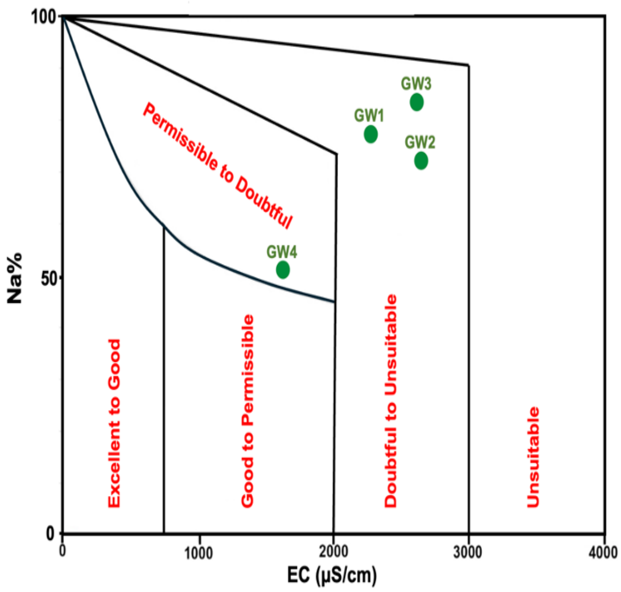

Figure 9. Wilcox diagram showing groundwater quality for irrigation.

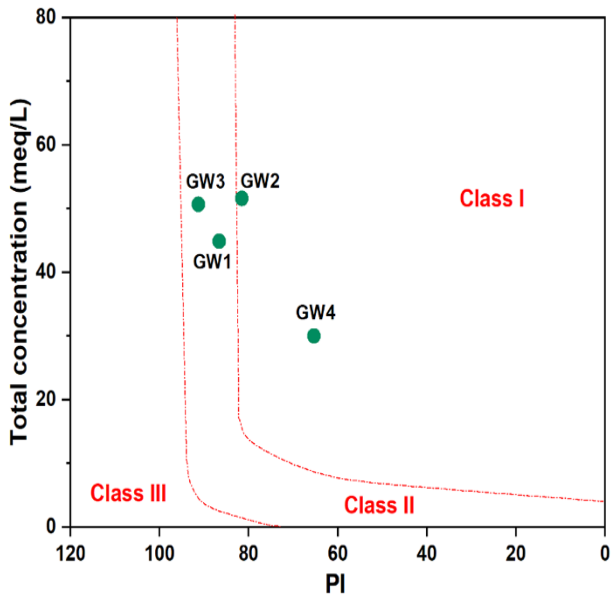

Figure 10. Classification of groundwater according to PI diagram.

3.3.9. Boron

Boron (B) is an essential micronutrient for plants that plays an important role in cell wall formation, carbohydrate translocation, plasma membrane structure stability, ion transport, flowering, fruit formation, and enhancement of cell division [74,75]. Boron is found in high concentrations in well waters, while it is generally found in surface waters at concentrations of 0.10–0.30 mg/L [76]. The narrow range between the optimum and toxic levels of boron for plants makes boron an important parameter for irrigation water [77]. In one study, it was reported that irrigation water containing 0.1 mg/L boron promoted the ripening of tomatoes in various soils and irrigation water containing up to 0.5 mg/L boron did not have any adverse effects on vegetables [78]. Another study reported that the application of more boron (> 1 mg/L) to bean plants than they need leads to inhibition of the plant's growth metabolism [77]. However, it is important to note that the susceptibility of plants to boron also depends on the plant species, and some plants may have a higher toxicity threshold for boron [79]. Based on boron concentrations in irrigation water up to 0.5 mg/L, 0.5–1 mg/L and >1 mg/L, irrigation water can be classified as "safe", "slight to moderate" and "severe", respectively [80]. In the study, the boron concentrations of GW1, GW2, GW3 and GW4 were 0.55, 0.79, 1.39, and 0.67 mg/L, respectively. According to boron concentration, GW1, GW2 and GW4 were classified as "slight to moderate" and GW3 was classified as "severe" due to boron concentration >1 mg/L.

3.3.10. Trace metal(loid)s

Table 3 shows the concentrations of metal(loid)s in groundwater samples, and Food and Agriculture Organization (FAO) guideline values for irrigation water. Concentrations of Pb, Cd, Co, and Cr in groundwater were <0.5 µg/L. Cu and Ni concentrations in all groundwater were <1 µg/L and <5 µg/L, respectively. Concentrations of Fe, Mn, Al, Zn, and As in groundwater ranged from 37.8–101, 9.7–15.3, <20–32.4, 1–5.86, and <0.5–1.1 µg/L, respectively. The concentration of metals in groundwater did not exceed the FAO guideline values for irrigation water.

Table 3. Concentrations of trace metal(loid)s in groundwater samples and FAO/WHO limit values.

	GW1 (µg/L)	**GW2 (µg/L)**	**GW3 (µg/L)**	**GW4 (µg/L)**	**FAO limit values for irrigation water (mg/L)** [81–83]	**WHO limit values for drinking water (mg/L)** [84,85]
Al	<20	29	<20	32.4	5	0.2
As	1.01	1.1	<0.5	<0.5	0.1	0.01
Fe	49.5	57.2	101	37.8	5	0.3
Mn	9.7	13	9.71	15.3	0.2	0.1
Ni	<5	<5	<5	<5	0.02	0.02
Cr	<0.5	<0.5	<0.5	<0.5	0.1	0.05
Cu	<1	<1	<1	<1	0.2	0.05
Co	<0.5	<0.5	<0.5	<0.5	0.05	0.05
Cd	<0.5	<0.5	<0.5	<0.5	0.01	0.003
Pb	<0.5	<0.5	<0.5	<0.5	5	0.01
Zn	5.86	2.08	1	1.54	2	3

3.3.11. Corrosivity ratio (CR)

The CR value is a parameter to assess the corrosivity of groundwater and is generally used to investigate the corrosive tendency of groundwater on metallic pipes [22,86]. A CR value of >1 is considered "unsafe" and <1 is considered "safe". Since all the groundwater in the studied area has a CR value >1 (2.23–7.67), the waters are prone to corrosion on pipes. Therefore, if these groundwaters are used for irrigation, metal pipes, valves, and fittings may undergo corrosion over time. Das et al. (2011 recommended the use of polyvinyl chloride (PVC) pipes for groundwater with a CR value >1 [22].

3.4. Weighted arithmetic water quality index

WAWQI is used to estimate the suitability of water for different purposes [87]. WAWQI is widely used to assess the quality of groundwater and surface water resources [88–91]. In this study, the WAWQI values of groundwater samples varied between 12.85 and 16.77 (Figure 11). Since the WAWQI value of all groundwater samples was <25, the quality rating of all groundwater was determined as "excellent". The WQI values of groundwater showed that groundwater is a very suitable source for drinking, industrial, and irrigation purposes [92]. The WAWQI values of all groundwater samples were below 25, indicating that the waters are in the "excellent" class in terms of overall quality. However, it should be noted that, as mentioned before, the WAWQI value is calculated considering pH, EC, TDS, major anions and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-) and metal(loids) (e.g. Al, As, Cd, Cr, Cu, Pb, Zn, Fe, Mn, Ni, B). Therefore, even though WAWQI values are low, some groundwater samples (e.g., GW1, GW2, and GW3) cannot be considered highly suitable for irrigation due to high salinity or sodium hazard according to the irrigation water quality indices. This demonstrated the need to consider a combination of quality indices in the assessment of groundwater use for different purposes.

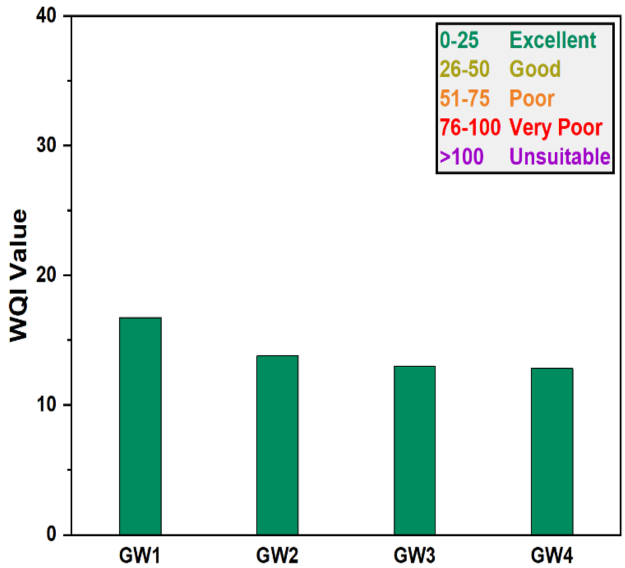

Figure 11. WAWQI value of groundwater samples.

3.5. Non-carcinogenic health risk assessment

Groundwater collected from wells in the study area is used for drinking and domestic purposes. The concentrations of trace metal(loid)s in the water are below the WHO drinking water limit values (Table 3). However, the long-term consumption of groundwater as drinking water leads to chronic exposure to multiple metals. Therefore, a health risk assessment was conducted to evaluate the potential effects of long-term oral exposure to metal(loid)s in groundwater through drinking water on human health. Table 4 presents the CDI, HQ, and HI values calculated for the trace metal(loid)s in the groundwater samples, to assess the non-carcinogenic health risks for both adults and children through oral exposure. The HQ values showed that As (from 4.57E-02 to 1.00E-01) caused the relatively highest risk for adults and Zn (from 9.13E-05 to 5.35E-04) caused the lowest risk. The HQ_{adults} value of all metals in all four well waters was <1, indicating that none of the metals posed a non-carcinogenic health risk to adults (No concern). The HI_{adults} values of all metals in the groundwater samples, calculated by taking into account the impact on health risk, were <1. This indicated that oral exposure of adults to all groundwater studied did not pose a non-carcinogenic health risk to adults.

The health risk of oral exposure to metals in groundwater was higher for children than for adults. This may be explained by children's lower tolerance to contaminants due to their lower body weight. The $HQ_{children}$ value calculated for metals in groundwater samples also revealed that As (from 1.07E-01 to 2.34E-01) caused the relatively highest risk and Zn (from 2.13E-04 to 1.25E-03) caused the lowest risk. The $HQ_{children}$ value of <1 for each metal in all groundwater samples indicated that the metals in these waters did not have the potential to pose a non-carcinogenic health risk to children (No concern). The $HI_{children}$ value for all groundwater samples was <1, indicating that the combined effect of the metals in the groundwater samples did not pose a non-carcinogenic health risk to children.

4. Conclusions

In this study, the chemical composition, hydrogeochemical characteristics, suitability for different uses, and non-carcinogenic risks to human health of trace metals exposed by ingestion were determined for groundwater in the Reyhanlı district of Hatay, the southernmost province of Türkiye. The dominant ion types in groundwater were Na^+ and Cl^-, while rock weathering and evaporation were the main mechanisms affecting groundwater chemistry. The WAWQI values of all groundwaters were in the range of 0–25, and the groundwaters were classified as "excellent" according to the WAWQI value. The WAWQI values showed that the groundwater is suitable for drinking, irrigation, and industrial applications. The pH and RSC values of all groundwater samples and the metal(loid) concentrations in all groundwater samples were suitable for agricultural irrigation. Among the groundwater samples, GW4 was more suitable for agricultural irrigation with lower EC, TDS, SAR, Na%, SSP, MH, and CR values. Considering the use of groundwater for drinking water supply, the concentrations of metal(loid)s in all groundwater samples did not exceed the WHO drinking water guideline values. HQ and HI analyses showed that the non-carcinogenic health risk due to oral exposure to metals was acceptable in all wells for both children and adults. In practice, groundwater with lower ion concentration and EC value (GW4) should be prioritized for agricultural irrigation and drinking water supply. The CR values of all groundwater samples were greater than 1; therefore, pipes made of corrosion-resistant materials should be preferred for well water transportation.

Table 4. CDI, HQ, and HI values for non-carcinogenic risk in adults and children.

	ADULTS							
	CDI_{adults}				**HQ_{adults}**			
	GW1	**GW2**	**GW3**	**GW4**	**GW1**	**GW2**	**GW3**	**GW4**
Al	5.48E-04	7.95E-04	5.48E-04	8.88E-04	5.48E-04	7.95E-04	5.48E-04	8.88E-04
As	2.77E-05	3.01E-05	1.37E-05	1.37E-05	9.22E-02	1.00E-01	4.57E-02	4.57E-02
Cd	1.37E-05	1.37E-05	1.37E-05	1.37E-05	2.74E-02	2.74E-02	2.74E-02	2.74E-02
Cr	1.37E-05	1.37E-05	1.37E-05	1.37E-05	4.57E-03	4.57E-03	4.57E-03	4.57E-03
Cu	2.74E-05	2.74E-05	2.74E-05	2.74E-05	6.85E-04	6.85E-04	6.85E-04	6.85E-04
Pb	1.37E-05	1.37E-05	1.37E-05	1.37E-05	3.91E-03	3.91E-03	3.91E-03	3.91E-03
Zn	1.61E-04	5.70E-05	2.74E-05	4.22E-05	5.35E-04	1.90E-04	9.13E-05	1.41E-04
Fe	1.36E-03	1.57E-03	2.77E-03	1.04E-03	1.94E-03	2.24E-03	3.95E-03	1.48E-03
Mn	2.66E-04	3.56E-04	2.66E-04	4.19E-04	1.90E-03	2.54E-03	1.90E-03	2.99E-03
Ni	1.37E-04	1.37E-04	1.37E-04	1.37E-04	6.85E-03	6.85E-03	6.85E-03	6.85E-03
Co	1.37E-05	1.37E-05	1.37E-05	1.37E-05	4.57E-02	4.57E-02	4.57E-02	4.57E-02
					HI_{adults}			
					1.86E-01	1.95E-01	1.41E-01	1.40E-01
	CHILDREN							
	$CDI_{children}$				**$HQ_{children}$**			
	GW1	**GW2**	**GW3**	**GW4**	**GW1**	**GW2**	**GW3**	**GW4**
Al	1.28E-03	1.85E-03	1.28E-03	2.07E-03	1.28E-03	1.85E-03	1.28E-03	2.07E-03
As	6.46E-05	7.03E-05	3.20E-05	3.20E-05	2.15E-01	2.34E-01	1.07E-01	1.07E-01
Cd	3.20E-05	3.20E-05	3.20E-05	3.20E-05	6.39E-02	6.39E-02	6.39E-02	6.39E-02
Cr	3.20E-05	3.20E-05	3.20E-05	3.20E-05	1.07E-02	1.07E-02	1.07E-02	1.07E-02
Cu	6.39E-05	6.39E-05	6.39E-05	6.39E-05	1.60E-03	1.60E-03	1.60E-03	1.60E-03
Pb	3.20E-05	3.20E-05	3.20E-05	3.20E-05	9.13E-03	9.13E-03	9.13E-03	9.13E-03
Zn	3.75E-04	1.33E-04	6.39E-05	9.84E-05	1.25E-03	4.43E-04	2.13E-04	3.28E-04
Fe	3.16E-03	3.66E-03	6.46E-03	2.42E-03	4.52E-03	5.22E-03	9.22E-03	3.45E-03
Mn	6.20E-04	8.31E-04	6.21E-04	9.78E-04	4.43E-03	5.94E-03	4.43E-03	6.99E-03
Ni	3.20E-04	3.20E-04	3.20E-04	3.20E-04	1.60E-02	1.60E-02	1.60E-02	1.60E-02
Co	3.20E-05	3.20E-05	3.20E-05	3.20E-05	1.07E-01	1.07E-01	1.07E-01	1.07E-01
					$HI_{children}$			
					4.35E-01	4.56E-01	3.30E-01	3.27E-01

Ethics committee approval and conflict of interest statement

This article does not require ethics committee approval.

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Author Contribution Statement

Seren Acarer Arat contributed to the conceptualization of the study, conducted the literature review, performed data analysis and calculations, interpreted the results, and carried out writing, reviewing, editing, and visualization. She performed the hydrogeochemical evaluation of groundwater, assessed its suitability for irrigation, calculated water quality index values, and conducted human health risk assessments for metals via the oral exposure pathway. Groundwater characterization data were provided by the General Directorate of Water and Sewerage Administration of Hatay Metropolitan Municipality.

Declaration of Generative AI

The author declares that a generative AI tool was used solely to improve the language of the manuscript.

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