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Research Article

Hydrochemistry and Entropy-Based Groundwater Quality Assessment in the Suining Area, Southwestern China

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Groundwater is an essential resource for sustainable development, whose quality is significant for human health. In the present study, twenty-eight groundwater samples were collected from domestic tube wells and public water supply wells in the Suining area, southwestern China. The integration of statistical analysis, correlations of ions, geomodelling, and entropy-weighted water quality index (EWQI) was carried out to clarify the hydrochemistry and groundwater quality in the study area. By the statistical analysis, the cations followed the concentration order as Ca^{2+}> Na^{+}> Mg^{2+}> K^{+}, while anions' concentrations were HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > F^-. Piper trilinear diagram showed the hydrochemical type was characterized as Ca-HCO_3. Correlations of ions and geomodelling revealed the concentrations of major ions were mainly determined by carbonate dissolution and ion exchange process, and NO_3^- concentrations were controlled by agriculture activities. EWQI computation demonstrated that most of the groundwater samples possessed EWQI values higher than 100. Therefore, groundwater quality is lower than the permissible limit of the World Health Organization (WHO), suitable for drinking purposes in the Suining area. Our study provides vital knowledge for groundwater management in the Suining and other similar areas.

1. Introduction

Groundwater is the basic and vital resource for humans living around the world. However, groundwater quality is deteriorating due to the rapid development of industrialization and urbanization, great growth of population, and excessive use of fertilizers [1–3]. So far, groundwater has been contaminated by nitrate, fluoride, arsenic, heavy metal elements, etc., seriously threatening to human health [4–8]. Comprehensive investigations of groundwater chemistry, mechanism analysis, and quality evolution can provide robust information for groundwater protection, which have been carried out globally [9–11].

Understanding groundwater chemistry is the critical fundament for mechanism analysis and quality evolution [12–14]. For numerous hydrochemical data, a statistical approach is used to analyse the general scope, which is shown in the Box-Whisker diagram [15]. The Piper trilinear diagram can present the water type clearly [16]. The mechanism for groundwater chemistry is mainly determined by natural processes and anthropogenic activities [17–19]. Natural processes generally consist of water-rock interaction, precipitation, and evaporation. Gibbs plots are regarded as the classic approach to distinguish the natural governing factors affecting groundwater chemistry [20]. Correlations of different ions and geomodelling can further constrain the rock type involving water [21]. Assessment of groundwater quality is a hot topic for numerous researchers. In the previous study, the traditional water quality index (WQI) was introduced to evaluate groundwater quality firstly [22–24]. Considering the various hydrochemical parameters, the WQI approach is not efficient to reveal the groundwater quality. The methodology for evaluating groundwater quality has experienced several stages from the traditional water quality index (WQI) to entropy water quality index (EWQI). The EWQI with entropy values involving various hydrochemical parameters has been believed to be a more robust approach due to its more comprehensive computation [19, 25–29]. In addition, the Geography Information System software (GIS) is helpful to reveal the spatial distribution of EWQI values. Therefore, the EWQI analysis has been extensively conducted for groundwater quality evaluation.

The Chengdu Plain is the area where industrialization and urbanization are rapidly increasing since the national developing strategy of the Chengdu-Chongqing economic circle was generated in the year 2020. The Suining area is an important city in the Chengdu Plain with a population of 3.6 million. The agriculture industry is active in the Suining area where the lands of 389 thousand hectares are exploited for extensive agricultural activity. However, scarce research has so far been conducted to understand the comprehensive evaluation of groundwater chemistry and quality from the Suining area. Therefore, the objectives of our study are as follows: (1) investigating the preliminary characteristics of groundwater chemistry, (2) identifying the factors controlling groundwater chemistry, and (3) evaluating groundwater quality using EWQI. The achievements of our study are hopeful to provide references for effective groundwater protection and management in future.

2. Materials and Methods

2.1. Study Area. The Suining area is located in the eastern part of the Sichuan Province, southwestern China, within the scope of E105°03′26″-106°59′49″ and N30°10′50″-31°10′50″ (Figure 1). The study area belongs to a subtropical humid monsoon climate with an annual temperature of 17°C and annual precipitation of 900 mm. The geomorphology is characterized as hilly and low mountain areas, with an elevation of 300–600 m. Rivers are developed in the Suining area where the Fu River is the dominant river (Figure 1).

The study area is situated in the Central Sichuan fold belt [30]. The strata are composed of the Quaternary sediments, Jurassic-Cretaceous calcareous mudstones and sandstones, and Triassic limestones (Figure 2) [31]. The Quaternary sediments contain sands, gravels, silty clay, and clay. The Jurassic-Cretaceous calcareous mudstones and sandstones consist of clay minerals (hydromica, kaolinite, and montmorillonite), detrital minerals (quartz, feldspar, and mica), and calcite. The Triassic limestones are dominated by calcite with less dolomite. Structures are not developed in the Suining area except for some E-W-trending wide folds. Groundwater mainly includes pore fissure water and fissure water and is recharged by infiltration of precipitation and local runoff. The Jurassic-Cretaceous calcareous sandstones are the main aquifers, while the mudstones are identified as confining beds [12]. The depth of groundwater is shallow and lower than 20 m. So far, groundwater has been exploited by local residents for domestic and irrigation goals.

2.2. Field Sampling and Laboratory Measurements. In this study, a total of twenty-eight groundwater samples were collected within the Suining area from groundwater wells during June 2016. Sampling sites were equally distributed in the study area. Prior to sampling, at least ten minutes were taken to pump stagnant water in the wells. Every sample bottle was rinsed three times by the sample water. All of the groundwater samples were analysed for hydrochemical compositions in the Laboratory of the Sichuan Provincial Bureau of Geology and Mineral Resources. Total dissolved solids (TDS) and major cations (e.g., K^+, Na^+, Ca^{2+}, and Mg^{2+}) were analysed by an atomic absorption spectrophotometer (AA6100; Techcomp, China). Cl^-, SO_4^{2-}, NO_3^-, and F^- were measured using ion chromatography (IC6100; Wayee, China). Chemical oxygen demand (COD) and total hardness (TH) and HCO_3^- were determined by titration. The charge balance error (CBE) ranged from −4.14% to +0.43% (calculated based on Equation (1)), validating the accuracy of experimental analyses:

$$\mathrm{CBE} = \frac{\sum \mathrm{cations} - \sum \mathrm{anions}}{\sum \mathrm{cations} + \sum \mathrm{anions}} \times 100\% . \tag{1}$$

2.3. Data Processing and Analysis. The statistical analysis for hydrochemical parameters was compiled based on SPSS 25. Piper diagram was drawn by AquaChem software version 3.0, showing the hydrochemical type.

The Materials and Methods section should contain sufficient detail so that all procedures can be repeated. It may be divided into headed subsections if several methods are described. The saturation index (SI) of specific minerals was computed using PHREEQC 3.0, based on the following equation:

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{K}\right), \tag{2}$$

where IAP represents ion activity in groundwater and K is the solubility constant under specific temperature.

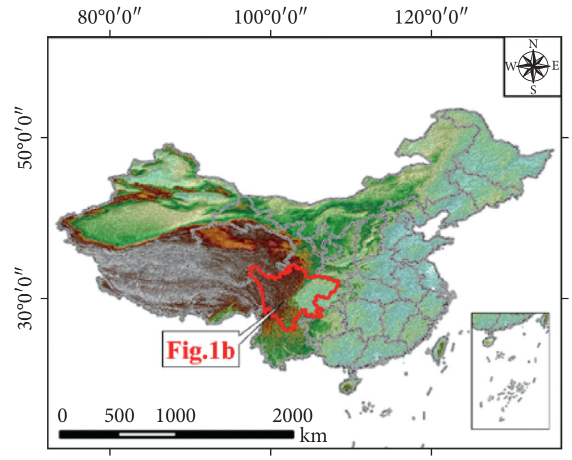
The entropy-weighted water quality index (EWQI) is the approach for evaluating water quality by entropy value involving various hydrochemical parameters. In general, the EWQI values were computed by four steps as follows:

Step 1: the eigenvalue matrix X is obtained as follows:

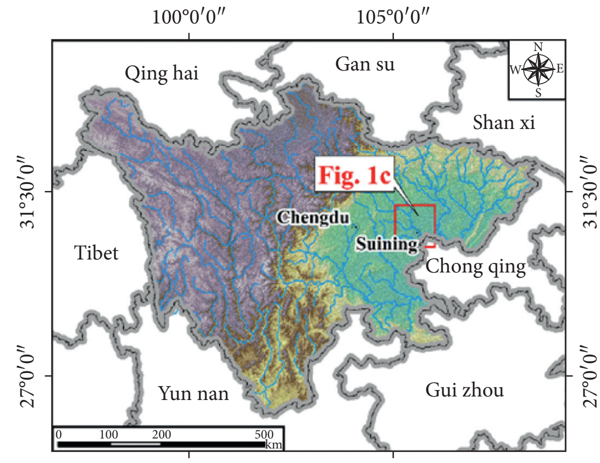
$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \cdots & x_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{bmatrix}, \tag{3}$$

where m is the total number of water samples and n signifies the number of hydrochemical parameters.

Step 2: the standard evaluation matrix "Y" is calculated as follows:



(a)



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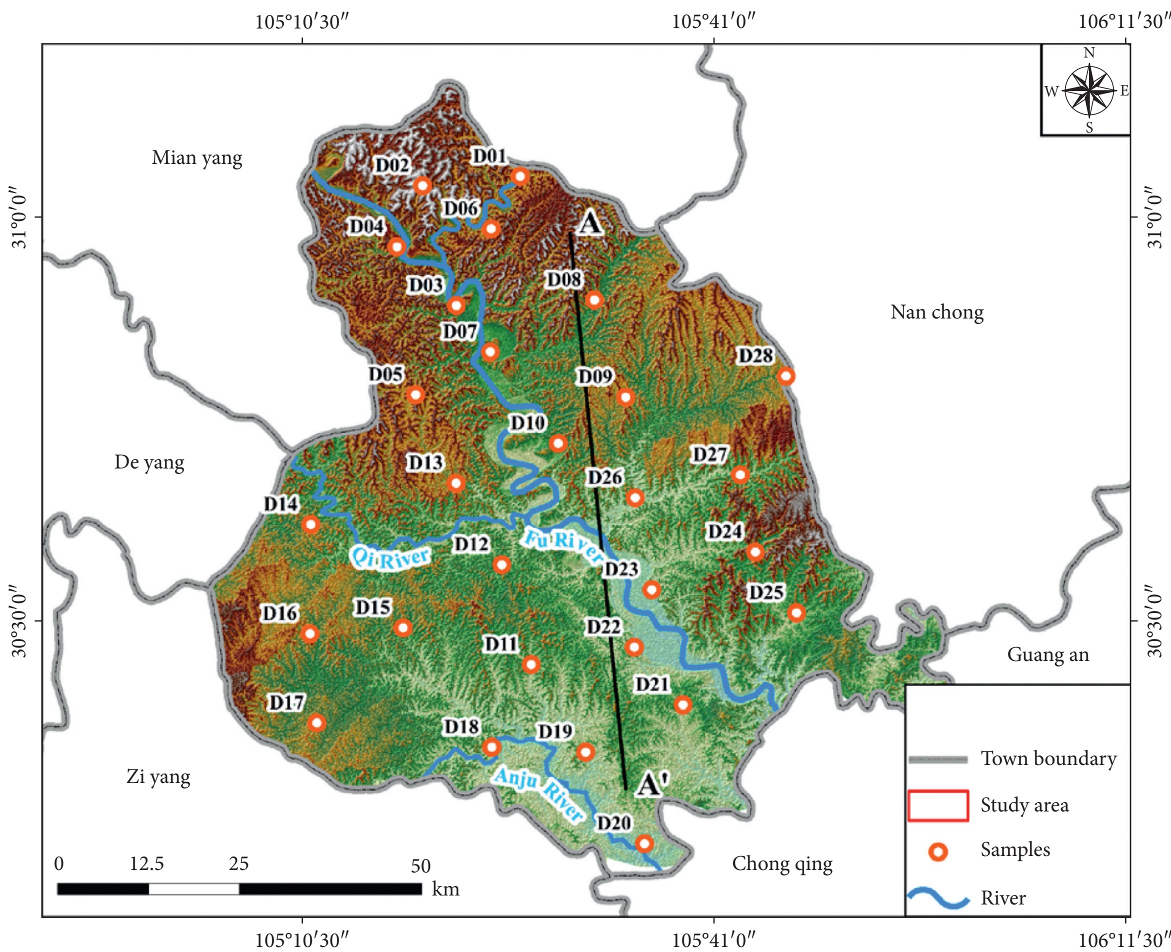


(c)

Figure 1: Study area location and sampling point distribution.

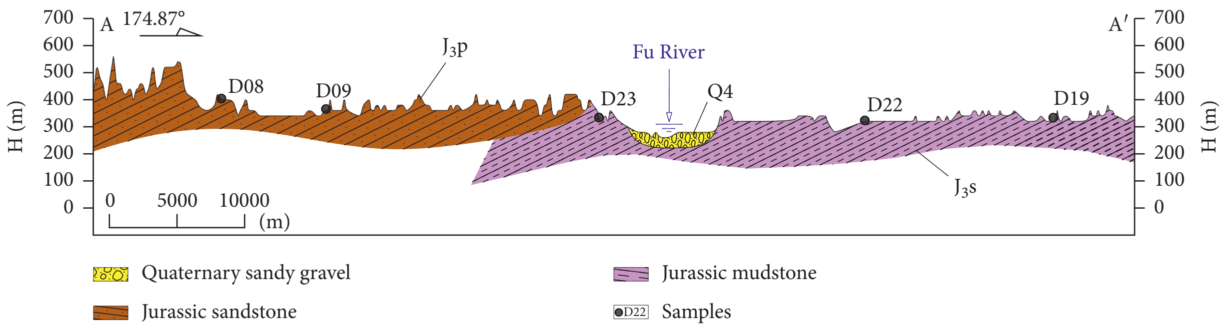


Figure 2: Geological section A-A' of the study area.

$$y_{ij} = \begin{cases} \dfrac{x_{ij} - (x_{ij})_{\min}}{(x_{ij})_{\max} - (x_{ij})_{\min}}, & \text{benefit type,} \\ \\ \dfrac{(x_{ij})_{\max} - x_{ij}}{(x_{ij})_{\max} - (x_{ij})_{\min}}, & \text{cost type,} \end{cases} \tag{4}$$

$$Y = \begin{bmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & \cdots & y_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ y_{m1} & y_{m2} & \cdots & y_{mn} \end{bmatrix}, \tag{5}$$

where $(x_{ij})_{\max}$ and $(x_{ij})_{\min}$ are the maximum and minimum values of the hydrochemical parameters of the water samples, respectively, and "y_{ij}" is the standardization process.

Step 3: the information entropy "e_j" is acquired as follows:

$$e_j = -\frac{1}{\ln m} \sum_{i=1}^{m} \left(P_{ij} \times \ln P_{ij}\right), \tag{6}$$

where P_{ij} is the parameter value ratio of parameter j for sample i, achieved based on Equation (6):

$$P_{ij} = \frac{y_{ij}}{\sum_i^m y_{ij}}. \tag{7}$$

Afterwards, the entropy weight "w_j" can be obtained as follows:

$$w_j = \frac{1 - e_j}{\sum_{i=1}^{n} \left(1 - e_j\right)}. \tag{8}$$

Step 4: the quality rating scale "q_j" of each parameter could be computed by the following equation:

$$q_j = \frac{C_j}{S_j} \times 100, \tag{9}$$

where C_j is the concentration of each hydrochemical parameter j and S_j represents the permissible limit of the World Health Organization standards for specific hydrochemical parameter j.

Finally, the EWQI value can be computed using the following equation:

$$\text{EWQI} = \sum_{j=1}^{m} \left(w_j \times q_j\right). \tag{10}$$

The classification of water quality based on EWQI is shown in Table 1.

3. Results and Discussion

3.1. General Characteristics of Groundwater Chemistry. The statistical results of hydrochemical parameters are presented in Table 2 and Figure 3, which were compared with the standard limits of the World Health Organization (WHO). The pH values varied from 7.1 to 8.4 (mean = 7.6), indicating neutral to slightly alkaline character and permissible for drinking purpose. Total dissolved solids (TDS) had concentrations of 20–830 mg/L, within the permissible drinking standard. The total hardness (TH) values ranged from 160.14 mg/L to 550.50 mg/L (mean = 389.99 mg/L). 17.86% of groundwater samples exceeding the permissible limit of 450.00 mg/L displayed the hard to very hard affinity (Figure 4(a)) and were unsuitable for drinking. Based on the statistical results, the major cations and anions followed the order of concentrations as follows: Ca^{2+} (46.10–184.40 mg/L) > Na^{+} (8.70–78.00 mg/L) > Mg^{2+} (6.10–42.60 mg/L) > K^{+} (0.90–25.00 mg/L), and HCO_3^{-} (140.30–530.90 mg/L) > SO_4^{2-} (45.90–207.00 mg/L) > Cl^{-} (7.20–90.50 mg/L). Ca^{2+} and HCO_3^{-} were the dominated cation and anion, respectively, characterized as the hydrochemical type of Ca-HCO_3 (Figure 4(b)). Most of the major ions (except Ca^{2+}) possessed concentrations less than the permissible limit for drinking purpose (Table 2). Of note, the NO_3^{-}, NO_2^{-}, and NH_4^{+} concentrations of groundwater samples were found beyond the permissible limit. Among them, NO_3^{-} had the highest concentrations of 0.20–244.00 mg/L, with 50% of groundwater samples exceeding the maximum allowable limit of 50 mg/L. NO_2^{-} and NH_4^{+} concentrations varied from 0.01 to 6.05 mg/L and 0.03 to 1.53 mg/L, within 18.57% and 11.43% of groundwater samples exceeding the permissible limit, respectively. Hence, nitrate contamination was identified in the Suining area. The F^{-} concentrations (0.2-0.6 mg/L) were obviously lower than the recommended level of drinking water standard.

Table 1: Classification criteria of water quality based on EWQI, according to reference [25].

Rank	EWQI	Water quality
1	<50	Excellent
2	50–100	Good
3	100–150	Medium
4	150–200	Poor
5	>200	Extremely poor

Table 2: Statistical results of hydrochemical parameters and drinking water standards.

Parameters	Max	Min	Mean	SD	CV (%)	Guideline	% of SEL
pH	8.4	7.10	7.6	0.25	3.37	6.5-8.5*	0.00
TDS	830	201	563	140	24.90	1000*	0.00
TH	550.50	160.14	389.99	89.04	22.83	450.00*	17.86
K^+	25.00	0.90	3.75	4.77	126.98	—	—
Na^+	78.00	8.70	31.66	14.81	46.76	200**	0.00
Ca^{2+}	184.40	46.10	118.68	30.67	25.85	75**	92.86
Mg^{2+}	42.60	6.10	22.75	8.68	38.14	50**	0.00
Cl^-	90.50	7.20	30.62	22.98	75.06	250*	0.00
SO_4^{2-}	207.00	45.90	93.60	42.20	45.09	250*	0.00
HCO_3^-	530.90	140.30	348.31	89.41	25.67	—	—
NO_3^-	244.00	0.20	68.12	61.42	90.17	50**	50.00
NO_2^-	6.05	0.01	0.43	1.41	327.39	0.02*	18.57
NH_4^+	1.53	0.03	0.23	0.30	129.05	0.2*	11.43
F^-	0.6	0.2	0.4	0.10	27.16	1.0*	0.00

SD, standard deviation; CV (%), coefficient of variation; *Chinese Guidelines [32]; **WHO Guidelines [33]; % of SEL, % of samples exceeding the acceptable limit.

3.2. Factors Controlling Groundwater Chemistry. The natural sources controlling ion concentrations generally include evaporation, rock weathering, and precipitation. Gibbs raised the classified diagram for distinguishing the different natural sources [34]. In the Gibbs diagram, all groundwater samples are plotted in the area of rock dominance (Figure 5), indicating that water-rock interaction is the natural process determining the ion concentrations of groundwater.

3.3. Sources of Major Ions

3.3.1. Correlation of Major Ions for Mineral Dissolution. The correlation of major ions has been extensively used to clarify the mineral types involving the water-rock interaction (Figure 6). When the dissolution of halite is the main process, the mole ratio between Cl^- and Na^+ is equal to one. Most of the groundwater samples plotted below the $y = x$ line, against the possibility of halite dissolution. The excess Na^+ concentration was probably derived from silicate dissolution or ion exchange. The dissolution of gypsum would lead to the molar ratio between SO_4^{2-} and Ca^{2+} equal to one. All of the groundwater samples drifted under the $y = x$ line. The dissolution of gypsum was unlikely to be the main natural process, implying there are possibilities that some processes contribute Ca^{2+}. In the Ca^{2+} vs. HCO_3^-, groundwater samples followed the $y = x$ line, implying the occurrence of calcite dissolution. Molar concentrations of Ca^{2+}, Mg^{2+}, Na^+, and HCO_3^- constructed by Gaillardet et al. (1999) have been considered as the efficient approach to evaluate the effects of carbonate rocks, silicate rocks, and evaporite rocks on the hydrochemical compositions [35]. In this study, groundwater samples fell in the zone between the carbonate rocks and silicate rocks. Hence, silicates and carbonates rather than evaporites had a contribution to groundwater chemistry. Accordantly, groundwater samples were distributed in the areas of silicate weathering and calcite dissolution.

Ion exchange has been reported as the natural process universally occurring in the groundwater system [36–38]. The relationship between $(Ca^{2+}+Mg^{2+}) - (SO_4^{2-} + HCO_3^-)$ and $(Na^+ + K^+ - Cl^-)$ can be employed to identify the ion exchange. The plots of groundwater samples displayed a negative correlation, revealing the ion exchange existed between Ca^{2+} and Na^+. Moreover, the chloroalkaline indices (CAI-I and CAI-I) are feasible to constrain the type of ion exchange. When the CAI-I and CAI-II values are higher than zero, reverse ion exchange occurs. In contrast, ion exchange is supported by the CAI-I and CAI-II values lower than zero. In this study, most of the groundwater samples possessed the CAI-I and CAI-II values lower than zero. Hence, ion exchange between Ca^{2+} and Na^+ was proposed in the study area.

3.3.2. Saturation Index for Estimating Possible Mineral Phases. Saturation index (SI) is viable to reflect the mineral equilibrium state in the groundwater system. In this study, saturation indices of calcite, dolomite, gypsum, and halite were computed by Phreeqc 3.0, as shown in Figure 6(i). The

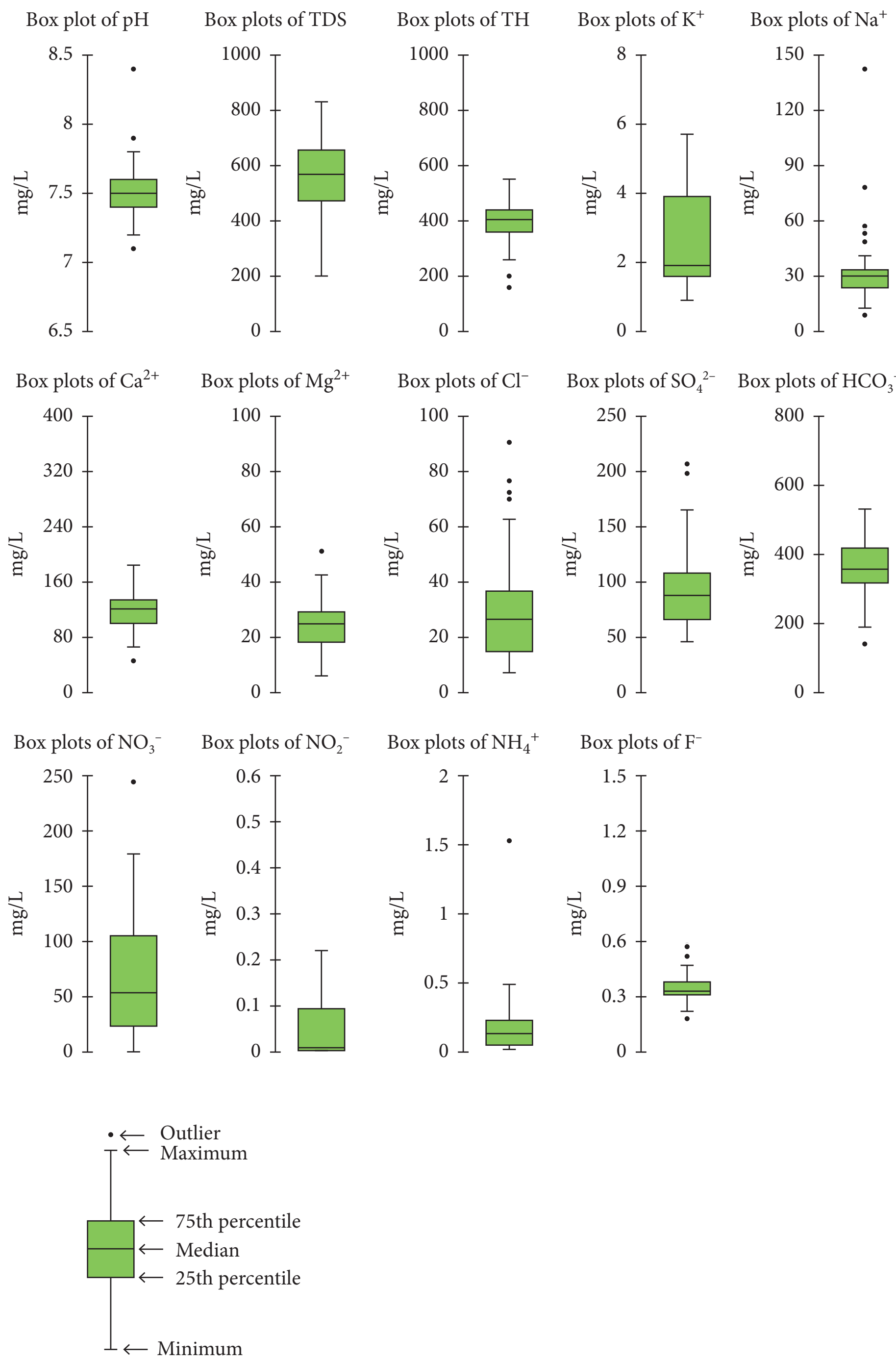
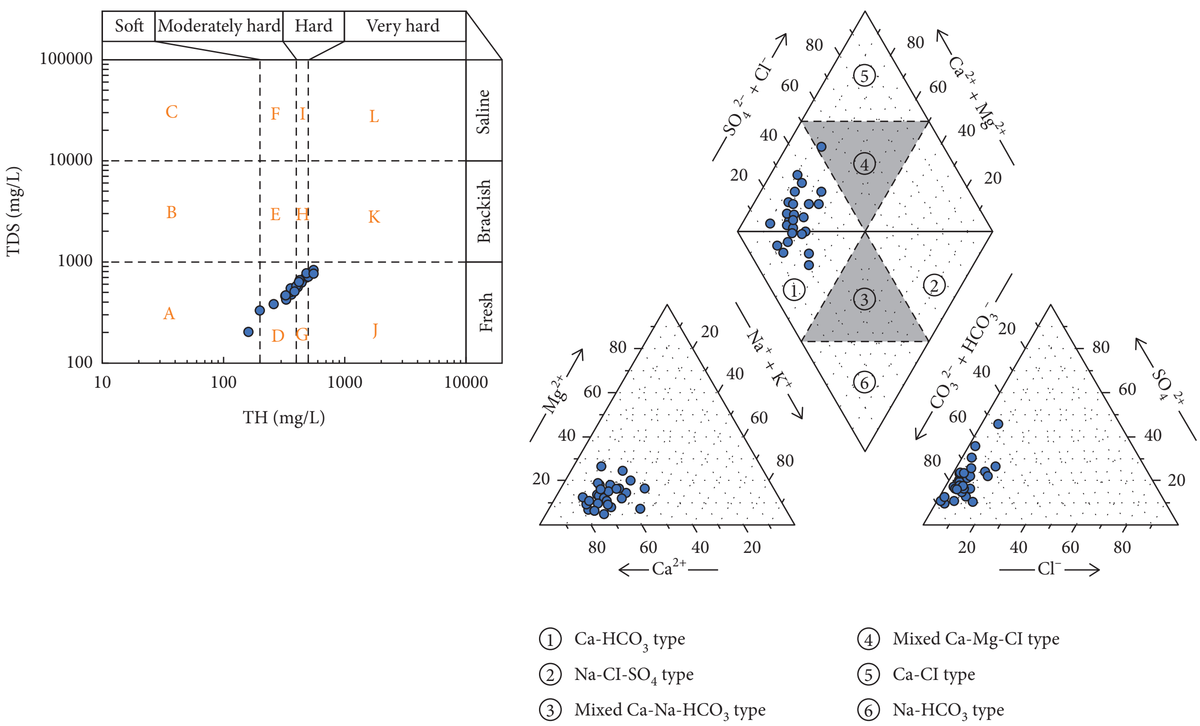


Figure 3: Box and Whisker plot of hydrochemical parameters of groundwater samples.

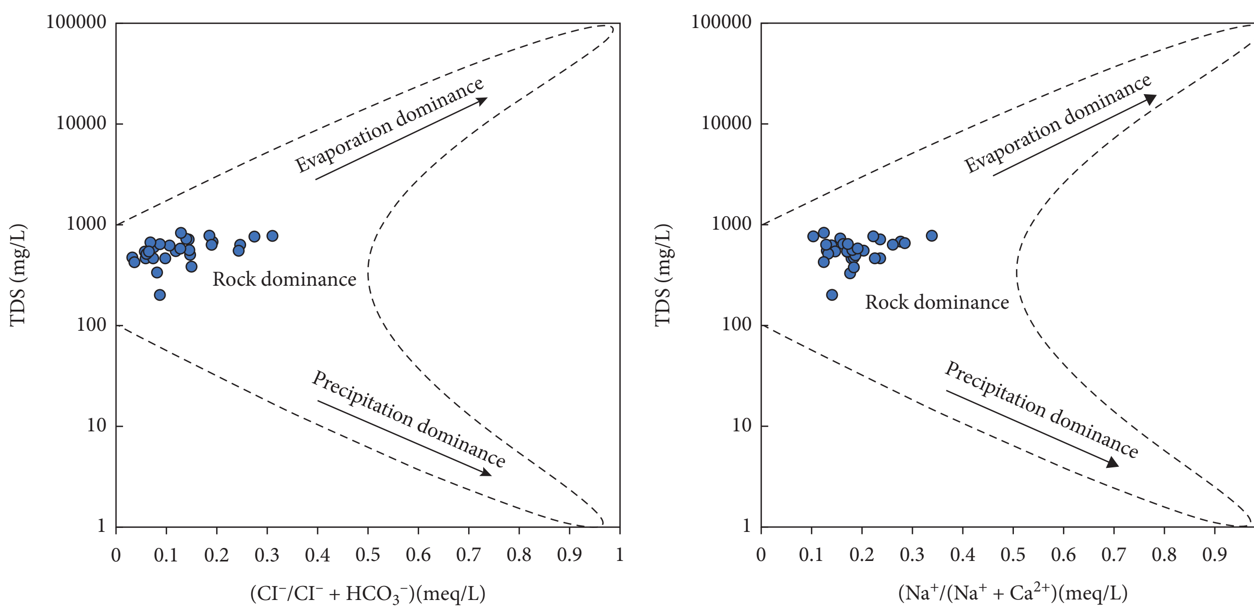
saturation indices of gypsum and halite were obviously lower than zero, implying the unsaturated state. Dolomite and calcite represented the oversaturated state by the saturation indices greater than zero. Hence, the hydrochemical compositions were mainly attributed to the dissolution of carbonate minerals.

3.3.3. Groundwater Quality Assessment Based on EWQI. The EWQI approach has been extensively used to evaluate the comprehensive effects of hydrochemical parameters on overall water quality [25, 26, 39]. The EWQI values lower than 100 imply that the water quality reaches the permissible limit for drinking purpose. In the present study, the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, F^{-}, NO_3^{-}, and TDS were involved in the computation of the EWQI. Herein, the EWQI values had a range of 95–235 (average value = 175) and were evaluated from rank 2 to rank 5 (Figure 7(a)). The majority of groundwater samples displayed the levels of Rank: 4 poor, lower than permissible drinking standard of the WHO.



(a) (b)

FIGURE 4: Scatter plots of (a) TH versus TDS demonstrating groundwater quality and (b) Piper trilinear diagram for groundwater samples.



(a) (b)

FIGURE 5: Gibbs diagrams demonstrating the mechanisms governing groundwater chemistry. (a) TDS *vs.* $Cl^-/(Cl^-+HCO_3^-)$; (b) TDS *vs.* $Na^+/(Na^++Ca^{2+})$.

The spatial distribution of the EWQI rank was visualized by the normal Kriging interpolation approach in the Geography Information System software (GIS) (Figure 7(b)). In Figure 7(b), the groundwater samples in the vast majority of the study area were not allowable for drinking purpose. Some local places in the western and middle parts of the study area had groundwater whose EWQI values largely exceeded the permissible limit for safe drinking. Therefore, the western and middle parts of the study area should be paid more attention for groundwater protection in future.

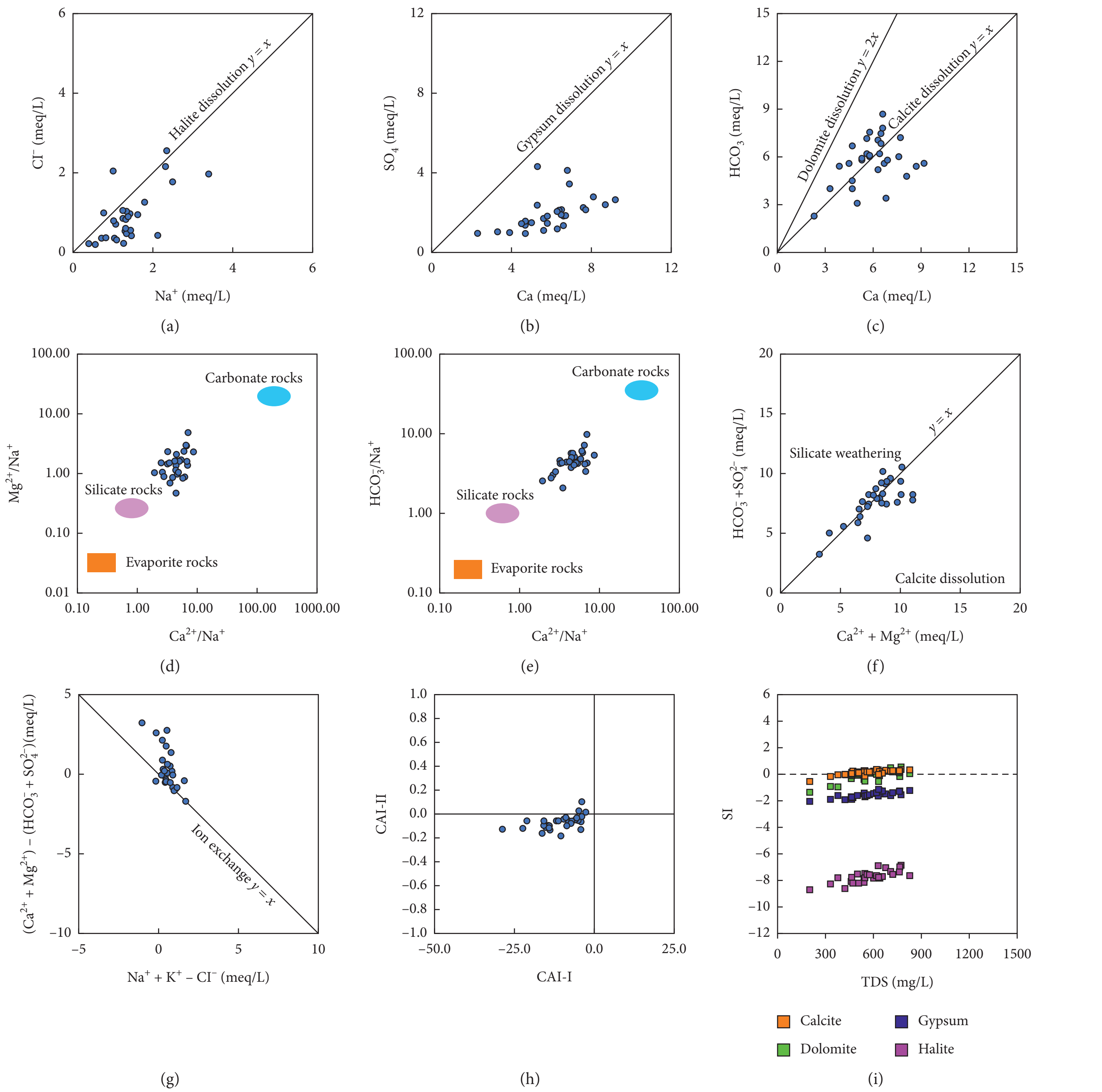
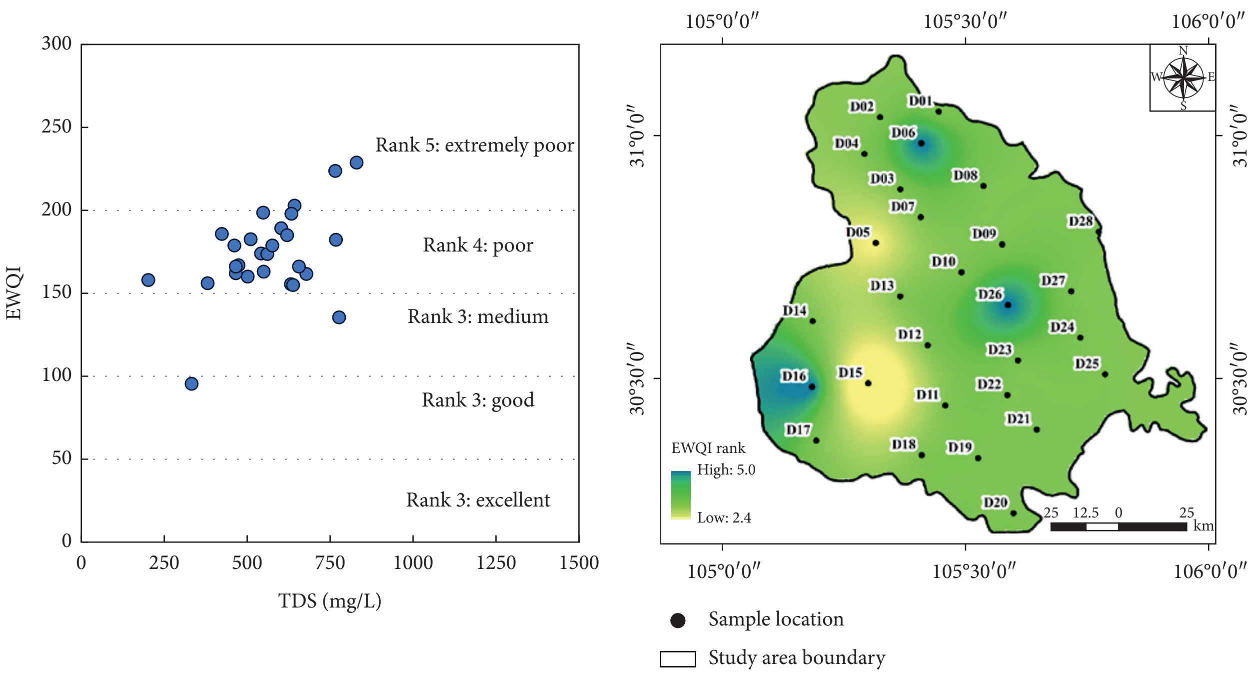


Figure 6: Correlation diagrams of (a) Cl^- *vs.* Na^+, (b) SO_4^{2-} *vs.* Ca^{2+}, (c) HCO_3^- *vs.* Ca^{2+}, (d) (Mg^{2+}/Na^+) *vs.* (Ca^{2+}/Na^+), (e) (HCO_3^-/Na^+) *vs.* (Ca^{2+}/Na^+), (f) $HCO_3^- + SO_4^{2-}$ *vs.* $Ca^{2+} + Mg^{2+}$, (g) ($Ca^{2+} + Mg^{2+}$) − ($HCO_3^- + SO_4^{2-}$) *vs.* $Na^+ + K^+ - Cl^-$, (h) chloroalkaline indices CAI-I *vs.* CAI-II, and (i) SI *vs.* TDS.



(a) (b)

Figure 7: (a) The relationship between the entropy-weighted water quality index (EWQI) and TDS and (b) spatial distribution of groundwater quality based on the EWQI rank.

4. Conclusions

In this study, twenty-eight groundwater samples were collected from the Suining area for hydrogeochemical analysis and quality assessment in order to better exploit and utilize groundwater resources. The main conclusions were drawn as follows:

(1) Groundwater samples represented alkaline affinity and high TDS values with Ca-HCO_3 type. The average cation and anion concentrations followed the order of $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > SO_4^{2-} > Cl^{-} > NO_3^{-} > F^{-}$. Nitrate contamination was identified by the NO_3^{-}concentrations of 0.20–244.00 mg/L.

(2) Ratios of major ions and geochemical modelling collectively revealed that hydrogeochemical compositions were dominated by carbonate dissolution and ion exchange.

(3) Entropy-weighted water quality index (EWQI) indicated that most of the total samples were unsuitable for drinking. The western and middle parts of the study area with higher EWQI values should be paid more attention for groundwater protection in future.

Data Availability

The data used to support the findings of the present study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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