

Article

# Assessing the Karst Groundwater Quality and Hydrogeochemical Characteristics of a Prominent Dolomite Aquifer in Guizhou, China

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Abstract: Karst groundwater is one of the primary water resources in most provinces of Southwestern China where karst topography is strongly featured. In Guizhou Province, a prominent geologic sedimentary formation is the dolomite stratum which exists as the restricted platform facies and potentially provides a large reservoir for drinking water. A proper understanding and evaluation of its hydrogeochemical characteristics and water quality is the key to ensuring the drinking water safety. In the present study, groundwater samples were collected from 25 locations of the dolomite aquifer across Guizhou to determine their major chemical compounds, including the cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>,  $Mg^{2+}$ ) and the anions (HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), as well as the pH, total hardness, and total dissolved solids.  $HCO_3^-$  and  $Ca^{2+}$  were found to be the dominant anion and cation, respectively, which is characteristic of typical karst groundwater and supports the overall observation of a slightly weak acid to weak alkaline environment in the studied groundwater, as the pH measurements ranged from 6.80 to 8.37. Fuzzy comprehensive evaluation method is used to evaluate the groundwater quality based on typical drinking water safety standard. The results show that the groundwater in most of the studied aquifers is of reasonably good quality. However, in some aquifers, concentrations of  $NO_3^-$  and/or  $SO_4^{2-}$  were found to be excessively high. Overall, the studied dolomite aquifer in its natural environment as investigated in the present study can be considered as a potential geological stratum for water resources exploitation in Guizhou.

Keywords: karst groundwater; hydrogeochemical; water quality; assessment; dolomite; aquifer

# 1. Introduction

Today, water scarcity remains one of the main challenges facing the modern world in the 21st century [1]; with continuous population growth and economic development, this threat is predicted to grow in the future [2]. Potential water shortage in karst mountainous areas is particularly significant due to its specific geochemical background and hydrogeological feature of karstic carbonate aquifers [3]. Karst topology occupies approximately 15% of the world's land area; one in every five persons depends on water from karst sources [4]. The evolution of geochemical compounds of karst groundwater is strongly affected by the karstification development [5–8]. Meanwhile, the hydrogeological structure of the karst formations may also considerably influence the geochemical processes in groundwater [6,9–13]. Guizhou Province is located at the center of southwest China, and nearly three fourths of its area is formed by karst landscapes; the dolomite stratum that exists as



the restricted platform facies is a key karst carbonate formation and may potentially provide a large resource for drinking water.

Karst water is especially vulnerable to environmental degradation which may impact neighboring aquifers unexpectedly. Numerous studies have been conducted to assess the integrity of karst systems to determine the water quality and sources of contamination and seek mitigation strategies. Environmental studies of the vulnerability of karst water are typically focused on two major types of implications, biological and chemical. For example, karst water has the potential to become carriers for waterborne diseases because the karst features have faster and convenient routes for the rapid flow of contaminants formed by the mineral dissolution [5,10,14,15]. In East Tennessee of the United States, 75% of wells and springs deriving water from either fractured sandstone or carbonate aquifers surveyed tested positive for E. coli (Escherichia coli), and both E. coli and total coliform bacteria were found in 63% of the samples tested [16]. Rosiles-Gonzalez et al. [17] found in a karst aquifer in the Yucatan Penisula, Mexico that indicators for fecal contamination include E. coli and pepper mild mottle virus. Heinz et al. [18] showed that the overflow events in combined sewer overflow systems resulted in levels of E. Coli 103 to 104 times higher than the background concentration at a karst spring in Gallusquelle, Germany. Boyer and Kuczynska [19] and Butscher et al. [20] have identified recharge events as crucial determinants in the vulnerability of karst regions to contaminants. Boyer and Pasquarell [21] studied the fecal bacteria in the karst groundwater aquifer influenced by agricultural activity in Appalachian Region where karst areas comprise about 18 percent of the region's land area.

The effluent from human and agricultural hubs also elicits chemical contamination. Fertilizers, animal wastes, and feed have contributed to the accumulation of nitrogen in a karst aquifer in Ireland under the influence of weather, farming practices, and local soil and geology characteristics [22]. A study carried out in Brazil showed that urbanization has a vital role on the quality of groundwater in an environmentally sensitive karstic watershed [23]. In the Kurnool District of Andhra Pradesh, India, the anthropogenic impact on karst water increases the concentration of trace metals [24]. Chemical degradation of karst aquifer in Yucatan peninsula of Mexico has decreased the availability of water for drinking and irrigation [25].

Karst groundwater quality in southwest China has also attracted growing attention in research communities. Especially, the rapid urbanization and industrial development driving increased human activities affect the dynamics of the karst water evolution in this region. Early studies by Yang [26,27] showed that the dominance of karst water with heavily concentrated CaCO<sub>3</sub> had gradually subsided, while high concentrations of CaMg(CO<sub>3</sub>)<sub>2</sub> had increasingly taken the place of calcium carbonate ions across Guangxi, Guizhou, and Yunnan Provinces. Yuan et al. [28] showed that the hydrogeochemical evolution of groundwater in Bijie City of Guizhou was mainly controlled by the dissolution/precipitation of carbonates, gypsum, and halite minerals, as well as cation exchange and anthropogenic activities. Zhang and Yuan [29] found that the land use and irrigation systems had altered the groundwater quality of Guizhou considerably; many underground water resources had been polluted by municipal and industrial wastewater disposal as well as excessive use of pesticide and fertilizer. Some detailed small-scale studies have been performed, mainly focusing on the city of Guiyang [30–33], which is the highly populated capitol of Guizhou Province. Many of the studies about the Guizhou's karst water revolve around the pollution of heavy metal concentrations resulting from the urbanization, industrialization, and mining processes [34–38].

Guizhou province is located in southwest China, between the geographical coordinates  $103^{\circ}36' \sim 109^{\circ}35'$  E and  $27^{\circ}37' \sim 29^{\circ}13'$  N. It is at the center of karst development in southwestern China. The karst area accounts for nearly three fourths of its total area [39], and its current population is around 34.8 million. It is of a subtropical warm–moist climate with an annual average temperature of 15.2 °C and an annual average relative humidity of 82%. The mean annual precipitation in the study area is around 110 cm;  $60 \sim 70\%$  of the precipitation occurs in May to October. The terrain elevation is high in the west and gradually decreases towards the east. The geological strata ranging from Middle Proterozoic to Quaternary are mainly marine carbonate strata which consist of three major types: the

dolomite stratum that manifests in the restricted platform facies, the limestone stratum in the open platform facies, and the limestone stratum in the reef facies. Of particular interest is the dolomite stratum widely distributed across Guizhou. It is concentrated primarily in the north and northeast, and sporadically in the central and south of Guizhou. As this karst stratum is characterized by a significant amount of dissolved pores and fissures, it is a major stratum targeted for karst groundwater exploitation in Guizhou. The present study is mainly motivated by the possibility of exploring this karst aquifer in this region. Typically, karst water evolves in a complicated manner shaped by the interplay between rock–water interaction, geological processes, and environmental changes as affected by human activities [40]. The present study aims to investigate the dolomite aquifer at its natural environment across Guizhou Province and offer a preliminary assessment of its quality and suitability for drinking water.

## 2. Hydrogeochemical Characteristics of Karst Groundwater

## 2.1. Groundwater Sampling and Testing in the Study Area

Groundwater samples were collected in 25 drilled boreholes in a field investigation that was performed across Guizhou between 2008 and 2012, as shown in Figure 1. The examined karst ground water were typically located in less-populated, rural areas under no evident influence of industrial or mining processes. The drilled boreholes were approximately 150 m-deep. Each groundwater sample was of 1.5 L and stored in a specialized container after the container was rinsed by the same water for  $3\sim5$  times. Subsequently, it was sealed with a membrane and kept in a constant temperature of 3 °C before it was transported to laboratory for testing. All samples were tested and analyzed within one month of the date of collection. The concentrations of the cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and the anions (HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), the total hardness, the total dissolved solids (TDS), and the pH value of each sample were measured. The pH tests were conducted in the field using the handheld equipment (Hanna HI98129 pH tester, Hanna Instruments, Smithfield, Rhode Island, USA); all other tests were carried out in the laboratory based on the national standard of China on the technical specifications for environmental monitoring of groundwater.

## 2.2. Results

Concentrations of various ions in all groundwater samples collected from the dolomite aquifer are detailed in Table 1, which also includes the results of the pH, the total hardness, and the total dissolved solids (TDS). The minimum, maximum, and mean values of these concentrations are also reported in Table 2. It is evident that the calcium cation  $Ca^{2+}$ , followed by significant concentration of magnesium  $Mg^{2+}$ , is the predominant cation in the groundwater, which is characteristic of typical karst aquifers. The bicarbonate ion  $HCO_3^-$  concentrations are the highest among all anions, except for Sample #22 where an unusually high concentration of sulfate ( $SO_4^{2-}$ ) was detected. Clearly, such high  $HCO_3^-$  concentrations are typical of carbonate rock aquifers such as the dolomite aquifer in the present study. Meanwhile, considerable presence of sulfates such as gypsums in Guizhou has been widely reported [41,42]. The  $SO_4^{2-}$  concentrations, while obviously lower than  $HCO_3^-$ , are still consistently higher than all other anions. In a few samples, relatively high concentrations of nitrate  $NO_3^-$  were found, indicating the possibility of natural nitrate salt deposit or agricultural use of fertilizers. Its presence may become a potential inhibitor for exploiting the studied karst groundwater as a drinking water resource.

The high concentrations of  $HCO_3^-$  also support the overall observation of a slightly weak acid to weak alkaline environment in the groundwater, as reflected by the pH measurements which range from 6.80 to 8.37 with a mean value of 7.39. The acidity in the groundwater of karst aquifers is mainly dictated by the geochemical interaction between water and rock, and usually exhibits complex dynamics between various processes including chemical reactions, mineralogical evolution, and hydrological processes. The observed narrow pH range of a very large studied area seems to suggest a

relatively stable existence of karst groundwater and aquifers in Guizhou, which may be potentially beneficial for long-term water resources exploitation.

 $Ca^{2+}$ ,  $Mg^{2+}$ , and  $HCO_3^{-}$  in karst groundwater are mainly derived from karst processes [5]; they form the dominant ions in karst groundwater. Correlations among these ions of all 25 collected groundwater samples are presented in Figure 2, where the molar concentrations (mmol/L) are used. It shows a fairly strong correlation between the concentrations of  $Ca^{2+}$  and  $Mg^{2+}$ , close to a ratio of 1:1, while the correlation between the concentrations of  $Ca^{2+}$  or  $Mg^{2+}$  and  $HCO_3^{-}$  is close to a 4:1 ratio. Therefore, it is noted that an electrical neutrality might be preserved, indicating these three ions might originate from the same source minerals and might be involved in the same geochemical and geohydrological processes. Similarly, the concentrations of  $Na^+$ ,  $K^+$ , and  $Cl^-$  are plotted in the correlation diagrams in Figure 3. The concentrations of the sodium and the chlorine are close to a 1:1 ratio and seem to suggest the rock salt (halite) as the main resource. The potassium concentration is far lower than the sodium concentration but still provides a fairly notable presence.

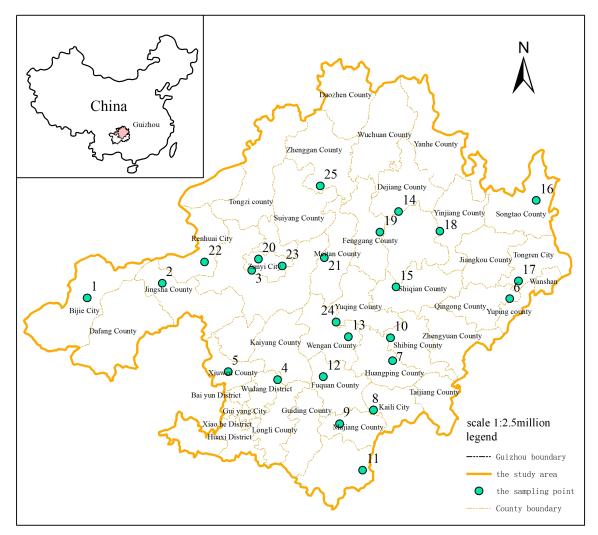


Figure 1. Map of the distribution of sampling locations in the study area of Guizhou, China.

Sample	pН	<b>Total Hardness</b>	TDS	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	$SO_4^{2-}$	$HCO_3^-$	$NO_3^-$	$\mathbf{F}^{-}$	$Cl^{-}$
1	7.30	184	293	40.0	20.4	1.02	0.80	5.85	222	0	0	2.51
2	7.32	334	333	74.9	35.7	1.93	1.33	14.5	392	2.67	0	5.56
3	6.80	331	355	81.2	31.2	1.33	2.33	71.3	302	4.00	0	6.21
4	8.14	202	316	40.7	24.4	1.26	1.55	5.77	232	7.48	0.07	2.71
5	7.27	287	427	60.2	33.4	1.29	1.47	20.8	289	15.5	0.25	5.04
6	7.50	421	410	8.41	50.3	0.33	1.67	16.0	485	0.60	0.20	7.44
7	7.80	328	423	70.1	37.3	1.13	1.86	20.6	343	34.7	0.05	7.44
8	7.30	293	447	60.3	34.8	0.46	0.76	17.4	311	20.7	0.09	1.90
9	7.74	259	408	49.8	32.5	0.76	0.58	10.7	304	7.68	0.06	1.73
10	8.37	283	447	57.7	34.0	0.20	0.53	6.42	333	8.33	0.10	4.57
11	7.30	277	277	60.6	30.4	0.67	2.00	10.0	319	3.00	0	5.61
12	7.20	306	341	65.5	34.5	2.00	3.00	80.0	241	26.0	0.20	4.68
13	7.30	286	295	60.3	32.9	0.33	2.00	28.0	311	6.00	0.06	4.21
14	7.10	285	283	61.1	32.2	1.00	1.33	16.0	322	2.00	0.20	2.15
15	7.30	335	333	70.1	38.7	0.33	2.33	12.0	385	5.00	0.40	6.61
16	7.50	347	358	40.8	17.8	1.00	4.67	30.0	176	2.00	0.24	3.74
17	7.40	236	236	48.5	27.9	0.67	1.67	14.0	259	4.00	0.10	4.92
18	7.40	286	283	63.4	31.1	0.33	3.33	12.0	311	10.0	0	7.49
19	7.80	229	242	60.1	19.0	1.33	2.00	22.0	249	4.00	0.04	4.21
20	7.30	244	271	70.8	16.3	1.00	2.33	45.0	225	10.0	0.10	6.55
21	7.30	308	315	64.2	35.8	0.33	0.67	24.0	342	10.0	0.06	1.87
22	7.10	743	937	197	60.9	2.67	3.33	420	289	96.0	0.30	5.66
23	7.30	285	301	63.2	31.0	0.67	1.33	10.0	304	7.67	0.12	3.30
24	6.90	425	439	84.6	50.9	2.00	3.00	60.0	441	4.00	0	7.80
25	7.20	338	377	81.2	32.8	1.67	8.67	47.0	339	16.0	0.10	14.5

**Table 1.** Geochemical concentrations in groundwater samples collected from the studied dolomite aquifer between 2008 and 2012 (all concentrations in mg/L), including the pH, total hardness, total dissolved solids (TDS), cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ), and anions ( $HCO_3^-$ ,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ).

**Table 2.** Statistics of geochemical concentrations in groundwater samples collected from the studied dolomite aquifer between 2008 and 2012 (all concentrations in mg/L), including the pH, total hardness, total dissolved solids (TDS), cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), and anions (HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>).

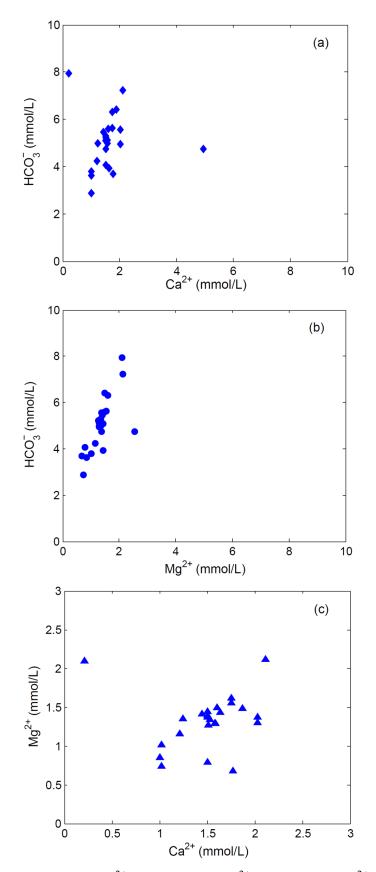
Sample	pН	Total Hardness	TDS	Ca <sup>2+</sup>	Mg <sup>2+</sup>	$\mathbf{K}^+$	Na <sup>+</sup>	$SO_4^{2-}$	$HCO_3^-$	$NO_3^-$	$\mathbf{F}^{-}$	C1 <sup></sup>
Min	6.80	184	236	8.40	16.3	0.20	0.53	5.77	176	0	0	1.73
Max	8.37	743	937	197	60.9	2.67	8.67	420	485	96.0	0.40	14.5
Mean	7.39	314	366	66.7	33.4	1.01	2.24	43.2	313	12.4	0.11	5.25

It is of interest to compare the total equivalent concentrations of anions and cations with previous research studies of other karst aquifers. In the present study of the dolomite aquifer, the total equivalent concentration of cations ranges from 3.73 to 15.07 meq/L with an average value of 6.39 meq/L. The total equivalent concentration range of anions was  $3.65 \sim 15.18$  meq/L, and its average value is 6.27 meq/L. Evidently, an electrical neutrality among the measured concentrations has been reasonably preserved. Several relevant findings reported in literatures are summarized in Table 3. Guo et al. [43] reported a mean value of 4.05 and 3.99 for cations and anions, respectively, in the karst groundwater of Guangxi province, a neighboring province to the south of Guizhou; these results are very close to those found in the south of Spain [44] and the northwest of Florida in the United States [45]. Elliot et al. [46] reported much higher concentrations in the confined fissured chalk aquifer of the London Basin of southern England. The present study shows the studied groundwater contains an abundance of mineral ions and the dolomite aquifer has a moderately active water–rock geochemical interaction.

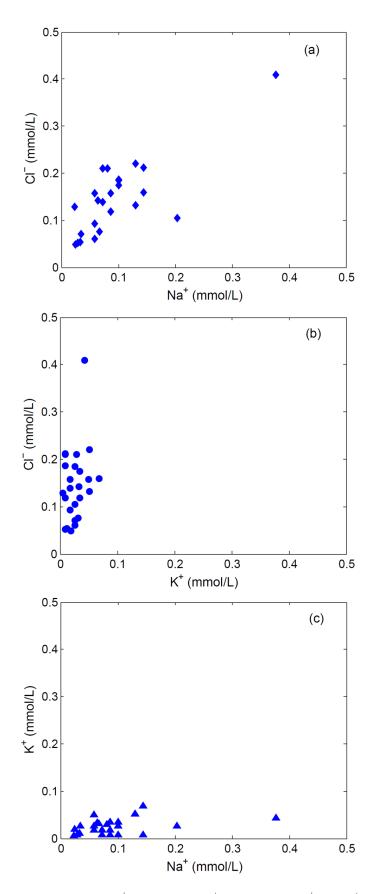
The experimental results are also analyzed in the well-known piper plot, i.e., trilinear piper diagram as presented in Figure 4. The trilinear piper diagram is commonly used in hydrogeology and groundwater analysis to show the percentage composition of different ions [47]. The water–chemical types of groundwater can simply reflect the main ions and their relative contents in water. The diagram consists of three components: a triangle in the lower left representing cations  $(Ca^{2+}, Mg^{2+}, and Na^++K^+)$ , a triangle in the lower right representing anions  $(Cl^-, SO_4^{2-}, and CO_3^{2-} + HCO_3^-)$ , and finally, a diamond plot in the middle which is a matrix transformation of the two triangles. Each concentration in a sample is normalized to 100% with respect to the total concentration, and the relative concentrations are on a percentage basis. For each sample, the two points in the two lower triangles are projected into a point in the upper diamond, this final location indicates the type of groundwater. Figure 4 shows nearly all samples fall into the category of calcium bicarbonate water  $(Ca \cdot Mg - HCO_3^{-})$ ; the only outlier is Sample #22 mentioned previously, which is a calcium sulfate water  $(Ca \cdot Mg - SO_4^{2^-})$ . The results are remarkably consistent, considering the large area investigated in the present study.

Karst Area	Average Equivalent Concentration of Cations (meq/L)	Average Equivalent Concentration of Anions (meq/L)	Data Source
Dolomite aquifer of Guizhou (China)	6.39	6.27	Present study
Karst aquifer of Guangxi (China)	4.05	3.99	Guo et al. [43]
Karst aquifer of Sierra de Segura (Spain)	4.03	4.28	Moral et al. [44]
Wakulla limestone aquifer of Florida (USA)	3.44	3.29	Katz et al. [45]
Chalk aquifer of southern England (UK)	8.33	8.01	Elliot et al. [46]

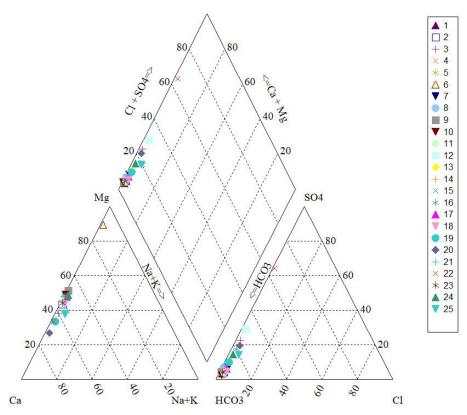
Table 3. Geochemical	characteristics of kars	st groundwater in	different karst areas.



**Figure 2.** Correlation between (**a**)  $Ca^{2+}$  and  $HCO_3^-$ ; (**b**)  $Mg^{2+}$  and  $HCO_3^-$ ; (**c**)  $Ca^{2+}$  and  $Mg^{2+}$  ions in the karst groundwater samples collected from the studied dolomite aquifer between 2008 and 2012.



**Figure 3.** Correlation between (a)  $Na^+$  and  $Cl^-$ ; (b)  $K^+$  and  $Cl^-$ ; (c)  $Na^+$  and  $K^+$  ions in the karst groundwater samples collected from the studied dolomite aquifer between 2008 and 2012.



**Figure 4.** The trilinear piper diagram for groundwater samples collected from the studied dolomite aquifer between 2008 and 2012.

#### 3. Assessment of Groundwater Quality with Fuzzy Comprehensive Evaluation Method

It is of interest to assess the quality of karst groundwater based on comprehensive evaluation which attempts to produce an overall evaluation from a set of individual evaluations [48]. The fuzzy comprehensive evaluation method is adopted in the present study, and the 25 water samples studied in the previous section are assessed.

#### 3.1. Evaluation Method

The concentrations of  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $Cl^-$ , $F^-$ , TDS, and total hardness are of pertinence to the safety of drinking water, and thus are chosen as the evaluation factors. Five classes from I to V are established for evaluation of each individual factor, as described in Table 4. The threshold values for each factor are selected based on the Quality Standard for Groundwater of China [49], where a higher threshold value, typically associated with higher class, indicates a lower water quality. Class I and II are typically associated with excellent and good water quality, respectively. Class III is considered to contain modest amounts of chemical content but of no harm to human health. Class IV can be used only for industrial or irrigational use but not suitable for drinking, Class V is considered obviously not potable and not even suitable for industrial or irrigational use.

The membership grade of the individual factor at all levels (I, II, III, IV, V) is determined by the following membership functions which are generally of a reduced semitrapezoid shape.

$$\mu_{i1} = \begin{cases} 1, & \text{if } 0 \le x_i \le a_1 \\ \frac{a_2 - x_i}{a_2 - a_1}, & \text{if } a_1 \le x_i \le a_2 \\ x, & \text{if } x \ge a_2 \end{cases}$$
(1)

$$\mu_{ij} = \begin{cases} 0, & \text{if } x_i \leq a_{j-1} \\ \frac{x_i - a_{j-1}}{a_j - a_{j-1}}, & \text{if } a_{j-1} \leq x_i \leq a_j \\ \frac{a_{j+1} - x_i}{a_{j+1} - a_j}, & \text{if } a_j \leq x_i \leq a_{j+1} \\ 0, & \text{if } x_i \geq a_{j+1} \end{cases}$$
(2)

$$\mu_{i5} = \begin{cases} 0, & \text{if } x_i \le a_4 \\ \frac{x_i - a_4}{a_5 - a_4}, & \text{if } a_4 \le x_i \le a_5 \\ 1, & \text{if } x \ge a_5 \end{cases}$$
(3)

 $\mu_{i1}$ ,  $\mu_{i2}$ ,  $\mu_{i3}$ ,  $\mu_{i4}$ , and  $\mu_{i5}$  are the membership (a "fuzzy value" between [0, 1]) of each single factor i, associated with Class I, II, III, IV, and V, respectively. It is noted that  $\mu_{i2}$ ,  $\mu_{i3}$ , and  $\mu_{i4}$  are defined via Equation (2) for j = 2, 3, 4. Evidently,  $a_1, a_2, a_3, a_4$ , and  $a_5$  are the threshold values under each class for each factor defined in Table 4. Consequently, the actual value  $x_i$  for factor i is then converted to a value between [0, 1] for subsequent assessment.

Index IV v No. Ι Π III 1 Total hardness 300 150 450 550 650 2 TDS 300 500 1000 2000 3000  $SO_4^{2-}$ 3 50 150 250 350 450 4 Cl-50 150 250 450 350 5 NO<sub>3</sub><sup>-</sup> 2 5 20 30 50 6 F<sup>-</sup> 1 1 1 2 3

Table 4. Class threshold values for groundwater quality evaluation (mg/L).

For each data point out of the 25 samples, there are a total of I = 6 factors, each of which is associated with J = 5 membership values for 5 classes. Therefore, a fuzzy relational matrix **R** of  $I \times J$  rank is established for each sample.

Subsequently, the intermediate weight of each factor can be calculated via

$$w_i = \frac{x_i}{c_0},\tag{4}$$

where  $w_i$  is the weight of Factor *i*;  $c_0$  is the average value of all threshold values for Factor *i*, equal to  $(\sum_i a_{ij})/J = (a_{i1} + a_{i2} + a_{i3} + a_{i4} + a_{i5})/5$ . Subsequently, all final weights need to be normalized viz

$$\bar{w}_i = \frac{w_i}{\sum w_i}.$$
(5)

Clearly, the sum of all weights  $\sum \bar{w}_i = 1$ , and these weights form a weight row vector (1 × 6). For all 25 samples, a weight fuzzy matrix (25 × 6) is established and hereafter denoted as **A**.

Finally, the evaluation for the entire samples set (25 samples) is rendered by the multiplication of the relationship matrix  $\mathbf{R}$  and weight matrix  $\mathbf{A}$ :

$$\mathbf{B} = \mathbf{A} \cdot \mathbf{R}.\tag{6}$$

The fuzzy evaluation matrix, **B** (25  $\times$  5) then provides the degree of quality level for each membership (Class I~V).

#### 3.2. Evaluation Results

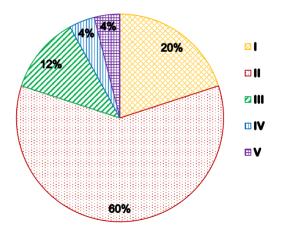
The evaluation results are presented in Table 5. Each "fuzzy" value in this table indicates the strength for the sample to be qualified as the prospective class. The final evaluation outcome is the one with the highest value.

Results summarized in Table 5 show that the groundwater form the studied dolomite aquifer is mainly Class II; almost 60% of samples fall in this category, indicating good quality as a drinking water resource. The percentage chart is shown in Figure 5. 20% of samples are classified as Class I with excellent quality. Only two samples are classified as clearly not drinkable, Sample #7 (Class IV) and Sample #22 (Class V). Sample #7 is located at Xinzhou town of Huangping County in the south of the study area. Its nitrate concentration is very high, far exceeding normal drinking water standard which considers 20 mg/L as the maximum acceptable concentration (Table 4). Sample #22 was collected from Tanchang town of Renhuai County in the north of the study area. As discussed earlier, it contains excessively high concentrations of nitrate and sulfate, and its total hardness is also very high. While the possibility of natural nitrate salt deposit or agricultural use of fertilizers may explain the presence of nitrate, the cause for its high total hardness may be related to the geochemical background of this dolomite aquifer in this region and worthy of further investigations. It is worth mentioning that the presented results are based on the commonly existing ions in typical karst water, possible heavy metal concentrations and other sources of potential pollution are not considered.

It should also be noted that although the present study considers only the Chinese national standard in the numerical model, the framework of the adopted method can be applied to other standards as well by using the specified threshold values. For example, WHO (World Health Organization) recommends 500 mg/L as the maximum acceptable concentration for total hardness, 600 mg/L for TDS, 50 mg/L for NO<sub>3</sub><sup>-</sup>, and 1.5 mg/L for F<sup>-</sup>; while the requirements for SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> are the same as in the examined standard.

Sample	Ι	II	III	IV	V	<b>Evaluation Outcome</b>
1	0.855	0.145	0	0	0	Ι
2	0.286	0.563	0.151	0	0	II
3	0.286	0.600	0.114	0	0	II
4	0.532	0.438	0.050	0	0	Ι
5	0.223	0.516	0.261	0	0	II
6	0.249	0.233	0.518	0	0	III
7	0.093	0.289	0.051	0.435	0.132	IV
8	0.119	0.409	0.423	0.032	0	III
9	0.289	0.609	0.100	0	0	II
10	0.180	0.763	0.057	0	0	II
11	0.404	0.596	0	0	0	II
12	0.216	0.319	0.192	0.273	0	II
13	0.360	0.626	0.013	0	0	II
14	0.482	0.518	0	0	0	II
15	0.326	0.557	0.117	0	0	II
16	0.386	0.438	0.176	0	0	II
17	0.579	0.421	0	0	0	Ι
18	0.245	0.647	0.108	0	0	II
19	0.607	0.393	0	0	0	Ι
20	0.454	0.444	0.102	0	0	Ι
21	0.228	0.648	0.123	0	0	II
22	0.024	0.010	0.068	0.058	0.840	V
23	0.299	0.655	0.046	0	0	II
24	0.231	0.299	0.470	0	0	III
25	0.225	0.424	0.351	0	0	II

**Table 5.** Results of fuzzy comprehensive evaluation of the quality of the collected groundwater samples, based on the fuzzy value of each class (I~V, Table 4); the class with the highest value indicates the final outcome of the quality.



**Figure 5.** Percentage charts of classifications (Class  $I \sim V$ , Table 4) of the quality of the collected groundwater samples.

# 4. Conclusions

The studied dolomite is a dominant geological karst stratum in Guizhou of Southwestern China and may potentially provide excellent water resources. The geochemical characteristics of this aquifer are investigated by studying collected groundwater samples collected from the natural environment in the field across Guizhou.  $HCO_3^-$  and  $Ca^{2+}$  were found to be the dominant anion and cation, respectively. Overall, the groundwater can be considered as calcium bicarbonate water (Ca  $\cdot$  Mg - $HCO_3^{-}$ ) based on its trilinear piper diagram. There were notable exceptions, mainly influenced by the presence of excessively high concentrations of  $NO_3^-$  and/or  $SO_4^{2-}$ . The presence of excessive nitrate strongly indicates the possibility of the influence of agricultural or other human activities in certain regions of the province, which overall is still under rapid urbanization and industrial development. A quantitative approach based on the fuzzy comprehensive evaluation method is adopted in the present study to assess the quality of the groundwater. The concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $F^-$ , TDS, and total hardness are the evaluation factors for the evaluation of the water quality. The numerical results show that most of the groundwater samples can be considered to be of good or excellent quality for drinking; however, it is noted that the presented results are based on the concentrations of commonly existing ions while concentrations of heavy metals or other harmful substances were not considered, as the examined samples were collected from less populated or industrialized areas in an attempt to study this type of aquifer in its natural environment. If sufficiently preserved to be immune from various sources of pollution, the studied dolomite aquifer has a great potential to be an important groundwater resource in Guizhou. Many studies have shown considerable water pollution as a consequence of various mining, urbanization, and industrialization processes, especially in the highly populated areas of Guizhou. Hence, further studies are still needed to better understand the dynamic of the evolution of this karst aquifer under the influence of anthropogenic activities in this rapidly developing region of southwest China.

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