

Article

Analysis of Hydrochemical Characteristics and Causes of Drinking Water Sources in South China: A Case Study in Zhanjiang City

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Abstract: The evaluation of groundwater environmental quality and the identification of recharge sources are very important for groundwater utilization. In this study, hydrochemistry and isotope analysis methods are used to investigate the recharge sources and hydrochemical processes of groundwater in Zhanjiang City. The results show that all samples of groundwater were drawn on the left of the global meteoric water line (GMWL: $\delta D = 8\delta^{18}O + 10$) and local meteorological water lines (LMWL1: $\delta D = 8.17\delta^{18}O + 11.74$ and LMWL2: $\delta D = 7.50\delta^{18}O + 6.18$), indicating that the groundwater was mainly recharged by meteoric precipitation and influenced by the effect of evaporation. In the middle and deep confined aquifers, the isotope data depleted with the depth, indicating that there is a relatively weak hydraulic connection between them. In addition, compared with unconfined groundwater, the isotope data of confined groundwater showed relative depletion, indicating that the confined aquifer may be partially recharged from other confined aquifers. The main chemical types in the groundwater were $Na^+Ca-HCO_3$. There are three major natural hydrochemical processes controlling the source of groundwater ions: silicate weathering, carbonate dissolution, and the cation exchange reaction. In addition, the differences in physical and chemical properties between unconfined groundwater and confined groundwater are significant. Due to the differences in anthropogenic activities and land-use types, the nitrate of the unconfined groundwater exceeds the groundwater standards. Due to the geological background of Zhanjiang City, iron and manganese exceed the third standard of groundwater in confined groundwater. Due to groundwater exploitation, TDS levels in confined groundwater have been increasing. Closed groundwater extraction is not sustainable, and it is depleting ancient water reserves. This study highlights the effectiveness of hydrochemistry and isotope analysis methods for identifying the recharge area and recharge mode of groundwater, and it is significant for fully understanding groundwater hydrochemistry and scientifically managing and protecting groundwater.

Keywords: groundwater; hydrochemical characteristics; stable isotope; factor analysis



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1. Introduction

Economic development intensifies the demand for freshwater worldwide [1]. As an important freshwater resource, the quality and quantity of groundwater have received much attention. Due to its wide distribution, a large amount of groundwater is used for

irrigation and industrial and domestic use. In China, approximately 400 cities exploit groundwater as a water resource [2]. Reports show that in approximately 220 cities in China, groundwater is used as drinking water resource. Most of this use occurs in the inland northwest part of China, where the environment is harsh and precipitation and surface water resources are scarce [3]. With the overexploitation of groundwater and the increase in anthropogenic activities, groundwater has faced serious environmental problems, including nitrate pollution, saline water mixing, the depletion of groundwater, and land subsidence [1,4]. The hydrochemical characteristics of groundwater are one of the important properties that determine the utility of groundwater resources. Researchers have studied the hydrochemical characteristics and recharge patterns of centralized, deep groundwater as a drinking water resource in parts of Northern China, such as Anhui and Fuyang [5,6]. Centralized deep groundwater in typical cities in Northwest China is affected by “rock weathering” and “evaporation.” Between these factors, evaporation is the main mechanism. In order to manage and exploit groundwater resources rationally, it is crucial to study the hydrochemical characteristics of deep groundwater [7–9].

Compared with inland cities, in which the environment is harsh, precipitation is scarce, and surface water resources are scarce, Zhanjiang City is located in the southwest of Guangdong Province, and its rainfall belongs to the rainbelt [10]. As most of the surface water flows directly into the sea and the resources are not evenly distributed in time and space, the surface water of Zhanjiang City is in relatively short supply. Groundwater has always been one of the main water sources of this city’s domestic, industrial, and agricultural production water. Since the 1950s, groundwater has become the central water supply source of Zhanjiang City. Due to the demand of economic development, groundwater extraction in Zhanjiang City has gradually increased, and the annual groundwater extraction accounts for about 50.60% of the total groundwater development and utilization in Guangdong Province [10]. There is a long history of groundwater development and utilization in Zhanjiang city, especially the concentrated and large-scale exploitation of middle and deep confined groundwater. Insufficient groundwater recharge and a drop in the water level have led to a series of ecological and environmental geological problems, such as groundwater level drop hopper, land subsidence, seawater intrusion, and groundwater pollution.

Hydrochemical characteristics reflect the environmental quality, the distribution of elements, and their migration/transformation [11,12]. The source of solutes in groundwater may be anthropogenic or natural [13]. Coupled with the input of artificial contaminants, the hydrochemical characteristics may change. Some activities may improve groundwater quality, while others cause groundwater pollution, such as nitrate and heavy metal contamination [5,14]. The major ions are widely used to identify the fundamental processes of water chemistry, such as the weathering of rocks in drainage basins, the evaporation/crystallization of water, atmospheric deposition, and interactions with anthropogenic influences [15,16]. Moreover, the hydrochemical characteristics of groundwater are mostly influenced by recharge sources, water–rock interactions, solute transport, and chemical processes [17,18]. In groundwater management studies, hydrochemistry and isotope-tracing methods are widely used to identify the recharge sources, recharge rates, and flow patterns of groundwater [19–22]. Therefore, with different recharge sources, hydrochemical and isotope indices also significantly differ, making them an effective “fingerprint” for studying groundwater recharge sources [23]. Yuan et al. discussed the runoff conditions of karst groundwater in Xianren Cave, Xichang, by using hydrochemical characteristics, ^2H , ^{18}O , and ^3H [24]. Jebreen et al. studied the recharge source of karst aquifer in Palestine by using ^2H and ^{18}O isotopes [25].

Groundwater can be divided into three types: unconfined groundwater (aquifer buried depth < 30 m), middle confined groundwater (buried depth of 30–200 m), and deep confined groundwater (buried depth of 200–450 m). Unconfined groundwater is usually replenished by rainfall and river runoff, and the water body circulates rapidly, causing it to be easily affected by anthropogenic factors [26]. In deep confined groundwater, storage is limited, the water circulation is slow, and the renewability is relatively weak [27].

Middle confined groundwater is between unconfined groundwater and deep confined groundwater [28]. The quality of unconfined groundwater in Zhanjiang City is affected by anthropogenic activities and environmental changes. The indices of ammonia nitrogen, iron, and manganese exceed the standards. Middle and deep confined groundwaters are buried deep, and the pollution degree is light due to the pollution isolation effect of the top waterproof layer, which mainly manifests as a high iron content.

A scientific understanding of the hydrochemical characteristics of groundwater in Zhanjiang City, analyzing and evaluating the current situation of groundwater quality, identifying the recharge area and recharge mode of groundwater drinking water source, and rationally developing and utilizing groundwater are of great significance for ensuring the sustainable utilization of groundwater resources. The aims of this study are: (1) to analyze and evaluate the current groundwater situation; (2) to reveal the hydrochemical evolution of unconfined, middle, and deep confined groundwater; and (3) to identify the source of the groundwater and the way through which artificial contamination may enter the groundwater.

2. Materials and Methods

2.1. Information of Study Area

Zhanjiang City is located in the southwest of Guangdong Province, China. Its annual average temperature, precipitation, and evaporation are 23.1 °C, 1620.0 mm, and 1189.1 mm, respectively. The groundwater drinking water resource in Potou District of Zhanjiang City, which can be used as the drinking water resource for the surrounding towns, was selected as the study area. The geographical coordinates are 110°25'12"–110°38'29" E and 21°11'24"–21°25'46" N. Combined with regional hydrogeological conditions and observation data, the scope of analysis of the hydrological recharge area is the Zhanjiang urban area, including tPotou District, Chikan District, Xiashan District, and Mazhang District, with a total land area of 1460 km². The geographical coordinates are 110°06'56"–110°39'23" E and 20°51'41"–21°27'28" N.

2.2. Sample Collection and Measurement

Fifteen groundwater sites were sampled in March 2022 to investigate the hydrochemistry of groundwater in Zhanjiang City. Fifteen groundwater samples were collected, comprising five unconfined aquifers (sample numbers starting with Q; used as well water or pumping water, generally for laundry and daily drinking by some residents), three middle confined aquifers (sample numbers starting with Z; used as pumping water) and seven deep confined aquifers (sample numbers starting with S; used as pumping water), as shown in Figure 1.

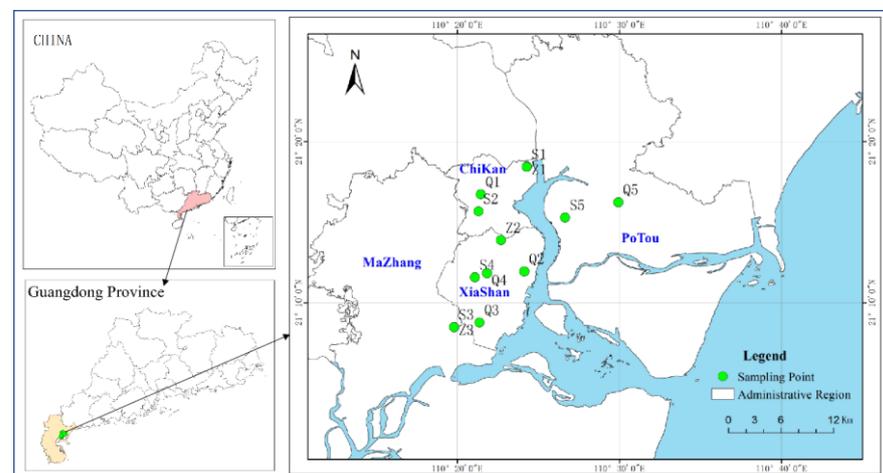


Figure 1. Location of the sampling sites.

For the collection of groundwater hydrochemistry samples, 100 mL brown polyethylene bottles were first cleaned. Samples were then collected three times. The bottles were sealed using a film, refrigerated in a timely manner in a refrigerator at 4 °C, and tested within 7 days. The concentration of major cations in the groundwater samples, including Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+), and Potassium (K^+), was detected by ICP-MS (ICP-MS, 7800 ICP-MS system, Agilent Technologies Co., Ltd., CA, USA). The pH, temperature, and total dissolved solid (TDS) content were measured immediately using a portable multiparameter water analyzer (HQ40d, HACH Co., Ltd., CO, USA). The concentration of HCO_3^- was determined by the titration method. The Cl^- , SO_4^{2-} , and NO_3^- were measured by ion chromatography (ICS 600 system, Thermo Scientific Dionex Co., Ltd., MA, USA).

To collect the groundwater isotope samples, groundwater was filtered through 0.45 μm membranes, stored in 10 mL glass bottles, and immediately sealed with a parafilm sealer to avoid evaporation. The $\delta^{18}\text{O}$ and δD of the water samples were measured in the Isotope Analysis Laboratory of the School of Environmental Science and Engineering, Sun Yat-sen University. The $\delta^{18}\text{O}$ and δD values were determined using a liquid water isotope analyzer (Delta Advantage V, Thermo Fisher Co., Ltd., MA, USA), with accuracy levels of 0.1‰ and 0.3‰, respectively. The measurements were expressed in terms of the Vienna Standard Mean Ocean Water as the thousandth difference [$\delta(\text{‰})$]. Isotopic ratios ($\delta^{18}\text{O}$ and δD) were calculated for standard samples as follows: $\delta_{\text{sample}} = (\delta_{\text{sample}}/\delta_{\text{standard}}) - 1 \times 1000(\text{‰})$, where δ_{sample} and δ_{standard} represent the ratio of heavy to light isotopes of the sample and standard, respectively. The results are shown in Figure 2.

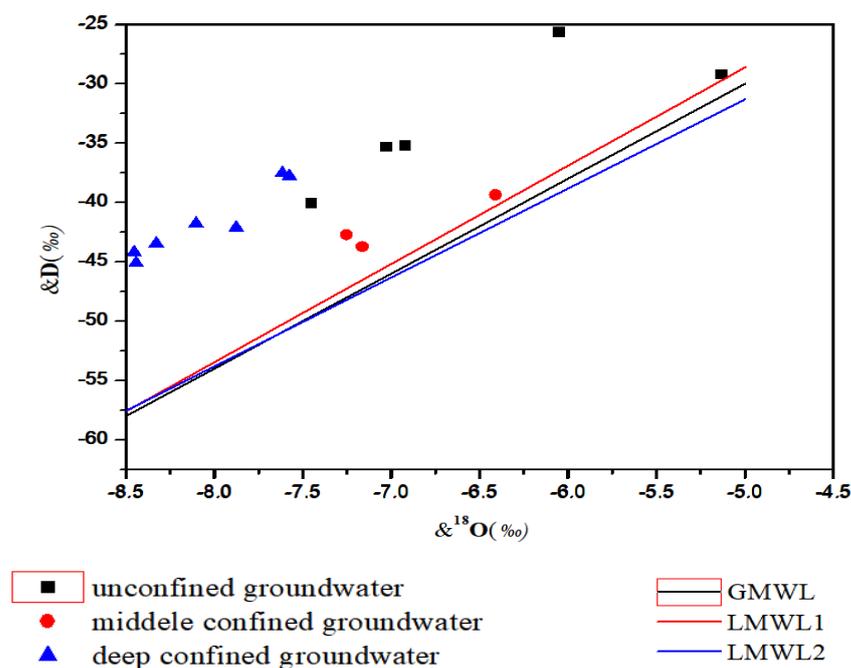


Figure 2. Stable isotopic compositions of groundwater in the study area.

3. Results and Discussion

3.1. Characteristic of Isotopes

The ^{18}O and D isotopes of the samples can reveal information about the water fluxes that are difficult to determine by other methods. Isotope analysis methods have been widely used in many hydrogeological studies [29]. The analytical results of the isotopes are shown in Table 1 and Figure 2. The isotopic compositions of ^{18}O and D were influenced by regional climate and local processes [30]. Based on the monthly rainfall data from the International Atomic Energy Agency's Global Network of Isotopes in Precipitation, the local meteorological water lines (LMWLs) of Hong Kong (LMWL1) and Haikou (LMWL2) stations could be calculated as $\delta\text{D} = 8.17\delta^{18}\text{O} + 11.74$ and $\delta\text{D} = 7.50\delta^{18}\text{O} + 6.18$,

respectively [31], which were regarded as the LMWL of Zhanjiang City. It can be found in Table 1 that the isotopic compositions of δD in the unconfined, middle, and deep confined groundwater were 25.56–40.00‰ (average of 33.01‰), 39.34–43.70‰ (average of 41.91‰), and 37.51–45.09‰ (average of 41.69‰), respectively. While the isotopic compositions of $\delta^{18}O$ in unconfined, middle and deep confined groundwater were 5.14–7.45‰ (average of 6.52‰), 6.41–7.25‰ (average of 6.94‰), and 7.58–8.45‰ (average of 8.06‰), respectively. The evaporation intensity of the unconfined, middle and deep confined groundwater was investigated by the deuterium excess values ($d\text{-excess} = \delta D - 8\delta^{18}O$). More negative $d\text{-excess}$ values implied a stronger evaporation effect [32]. It was found that the $d\text{-excess}$ values of the unconfined, middle and deep confined groundwater ranged from 11.96–15.33‰ (average of 13.21‰), 19.62–22.88‰ (average of 20.95‰), and 20.91–23.44‰ (average of 13.21‰), respectively. It was indicated that the ion contents of groundwater in Zhanjiang City were controlled by silicate weathering and influenced by carbonate dissolution and the cation exchange reaction.

Table 1. Summary of hydrochemical data in the study area.

	Sample ID	pH	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	K ⁺ (mg/L)	Na ⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	NO ₂ ⁻ (mg/L)	TDS (mg/L)
Unconfined aquifer	Q1	4.15	24.96	9.28	15.88	43.96	44.10	44.87	2.55	25.00	0.05	175.60
	Q2	7.02	115.19	10.28	27.48	62.44	29.98	3.49	180.97	9.00	7.42	169.41
	Q3	5.91	84.94	9.29	24.65	63.28	38.23	40.52	6.24	50.00	0.01	322.90
	Q4	7.21	128.72	18.43	72.48	19.85	50.25	70.93	281.17	35.00	0.02	239.80
	Q5	4.62	54.39	14.18	8.30	59.25	55.54	89.54	2.99	8.00	ND	216.32
Middle confined aquifer	Z1	6.39	29.31	4.23	22.75	11.76	2.66	19.72	61.74	ND	ND	92.10
	Z2	6.19	24.32	8.84	9.47	11.20	10.43	10.72	52.35	2.00	ND	109.23
	Z3	5.57	17.81	12.92	11.11	28.62	28.53	30.98	10.42	ND	ND	122.12
Deep confined aquifer	S1	8.11	15.59	1.01	6.18	227.90	5.19	7.15	251.52	ND	ND	332.40
	S2	6.61	14.24	5.31	18.65	18.52	16.84	8.34	92.65	0.60	ND	136.02
	S3	6.32	21.69	11.29	12.63	23.93	17.38	14.30	138.29	ND	0.02	212.18
	S4	6.65	22.65	11.25	14.71	17.84	4.43	5.96	95.59	0.60	ND	142.58
	S5	6.43	15.91	5.34	20.17	13.72	24.15	12.98	50.72	ND	ND	199.88
	S6	6.42	24.13	3.87	16.30	29.24	15.07	1.19	91.18	9.00	0.01	226.08
	S7	6.51	23.85	3.24	17.42	33.78	3.49	3.59	73.11	ND	ND	167.58

The different hydrogen and oxygen isotopic compositions of the surface water and groundwater in different layers could indicate the difference in the recharge sources and water cycle process, and the interaction relationship between them to a certain extent [33]. As shown in Figure 2, compared with the confined groundwater, the unconfined groundwater is the most enriched in isotopes. In addition, all samples of unconfined groundwater were on the left of the global meteoric water line (GMWL: $\delta D = 8\delta^{18}O + 10$), LMWL1, and LMWL2, indicating that the groundwater was mainly recharged by meteoric precipitation and influenced by the effect of evaporation. For confined aquifers, the isotope data depleted with the depth, indicating that the hydraulic connection between the middle and deep confined aquifers is relatively weak. The samples were drawn along the GMWL and LMWL, indicating that the confined groundwater originated from precipitation. However, compared with the unconfined groundwater, its isotope data was relatively depleted, indicating that the depletion of the precipitation isotope data may partially recharged from other middle and deep confined aquifers.

3.2. Hydrochemical Characteristics

Understanding the basic characteristics of groundwater chemistry is the basis for investigating groundwater sources and hydrochemical processes. The hydrochemical data of Zhanjiang City are shown in Table 1. In unconfined groundwater, the TDS ranged from 169.41 mg/L to 322.90 mg/L, with an average of 224.81 mg/L. There was a range of 92.10 mg/L to 122.12 mg/L in middle confined groundwater, with an average of 107.82 mg/L, while deep confined groundwater had a TDS of 202.39 mg/L on average, ranging from 142.58 to 332.40 mg/L. The TDS of all groundwater samples was within the desirable limit of 1000 mg/L provided by the Chinese Guidelines, indicating that the groundwater in this aquifer system is predominantly freshwater [34]. The humid climates

in Zhanjiang City could replenish groundwater by precipitation. The natural flow of the groundwater level above the mean sea level is the main reason that most unconfined groundwater is not salinized. In addition, the confined groundwater level is higher than the sea level, thereby preventing seawater intrusion into the confined groundwater.

The pH of the unconfined groundwater varied widely, ranging from 4.15 to 7.21 and averaging 5.78. Meanwhile, the middle confined groundwater had a pH ranging from 5.57 to 6.39, with an average of 6.05, while the deep confined groundwater had an average pH of 6.72, ranging from 6.32 to 8.11. With the increase in the depth of the groundwater, the pH slightly increased, which could be ascribed to the influence of anthropogenic activities. Additionally, Chinese guidelines recommend a groundwater pH range of 6.5–8.5 for drinking water sources; however, most groundwater samples were below that range [35]. Therefore, the groundwater is generally acidic, and the pH of the unconfined groundwater was higher than that of middle and deep confined groundwaters.

Among the cations, Ca^{2+} was the dominant ion in unconfined and middle confined aquifers, with concentration ranges of 24.96–128.72 and 17.81–29.31 mg/L, respectively. The Ca^{2+} in groundwater may come from the rock dissolution [36]. Meanwhile, Na^+ was the dominant ion in the deep confined aquifer, with a concentration range of 13.72–227.90 mg/L. Different to Ca^{2+} , rock–water interactions, the mixing of saline water, and ion exchange in similar regions induced Na^+ [37]. Seawater intrusion may be an important reason for the high concentration of Na^+ in the deep confined groundwater. Unconfined and middle confined aquifers had the following mean concentrations of major cations: $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$, while the deep confined groundwater followed the order $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ for its main cations. For anions, the order of mean concentration of these three major anions was $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. Due to the differences in anthropogenic activities and land-use types, the nitrate concentration in the unconfined groundwater exceeded the groundwater standards [38]. Nitrates can come from different sources, such as the excessive use of nitrogen-containing fertilizers and manures, domestic wastewater, and poorly maintained wells and sewers [39]. The changes in the TDS, major ions, and nitrates in groundwater were found to be related to human activities, such as agricultural practices (irrigation and fertilization), wastewater discharge, and groundwater extraction [40,41]. In addition, iron and manganese contents exceeded the third standard of groundwater in confined groundwater, which could be ascribed to the geological background of Zhanjiang City.

3.3. Hydrochemical Pattern of Groundwater

A Piper plot can aid in the understanding of a hydrochemical pattern and the underlying processes that control the hydrochemical characteristics of groundwater. The major ion concentrations shown in Table 1 were plotted, as shown in Figure 3. The distribution of water samples was close to the Na + K line and the Ca line and far from the Mg end. Thus, the main chemical types in groundwater were $\text{Na}^+\text{Ca}\text{-HCO}_3$, which is a typical feature of recharge water sources [42]. The formation and enrichment of Na^+ are mainly related to the water-bearing middle and overlying soil layer. As the aqueous middle in Zhanjiang City contains many clay minerals, Na^+ is subjected to ion exchange, the Ca^{2+} and Mg^{2+} in water are replaced with Na^+ , and the same amount of Na^+ is released into the groundwater, leading to the increase in its content and the high occurrence of Na^+ . Precipitation had been speculated to carry wastewater into groundwater and to promote the dissolution of rocks by the CO_2 it takes [43]. It had been reported that the concentration of major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and the HCO_3^- (alkalinity) concentration are increased by enhancing the CO_2 -mediated silicate mineral weathering [44]. The anion triangle at the bottom right shows a large difference, with Q1, Q3, Q5, and Z4 water samples near the SO_4^{2-} end and the remaining water samples near the $\text{CO}_3^{2-} + \text{HCO}_3^-$ end. HCO_3^- is mainly derived from the dissolution of carbonate rocks [1] and some compound fertilizers, such as NH_4HCO_3 [45]. In addition, the dissolution of CO_2 in the atmosphere and soil and the biodegradation process could cause a small part of CO_2 to enter the water body and

recharge the groundwater. This finding was consistent with previous studies, which found that the hydrochemical composition of the shallow groundwater is affected by the surface water and that the water quality of the deep groundwater is stable [46].

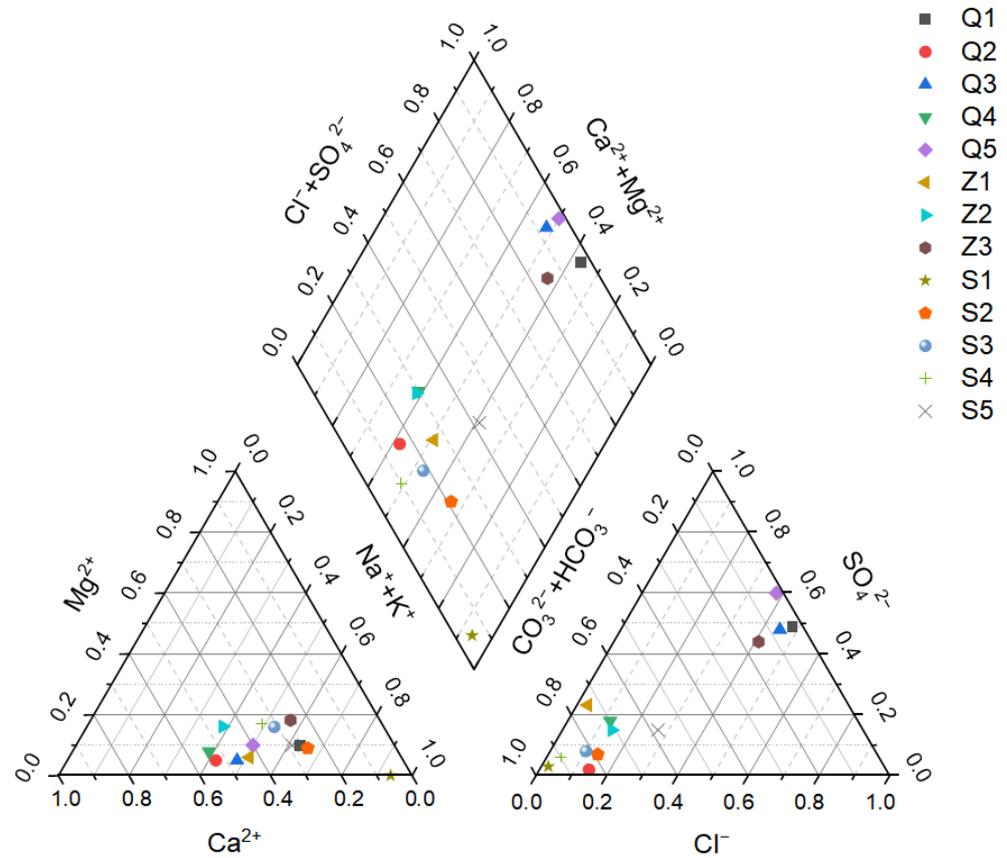


Figure 3. Piper diagram of chemical compositions for groundwater.

By using the Gibbs diagram [47], the relationship between the TDS and cation ratio $Na/(Na + Ca)$, and anion ratio $Cl/(Cl + HCO_3)$ could be assessed to determine the mechanisms controlling the groundwater chemistry [48,49]. As shown in Figure 4, the Gibbs diagram indicated that most of the samples had high $Na/(Na + Ca)$ and low $Cl/(Cl + HCO_3)$ levels and moderate TDS, of which the majority of samples were plotted in the rock-dominant zone, whereas the evaporation-dominant zone and the precipitation-dominant zone had very few samples. The results also revealed that water–rock interactions determine the hydrochemical characteristics of groundwater, followed by evaporation and precipitation.

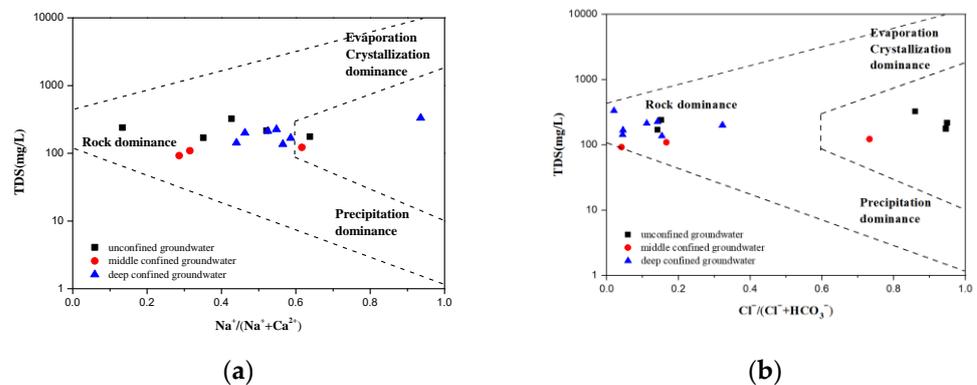


Figure 4. Gibbs diagram for (a) cation ratios and (b) anion ratios.

3.4. Correlation Relationship

The relationship between major ions and TDS could be used to investigate the major hydrogeochemical evolution processes occurring in groundwater and to determine the source of the ions in groundwater [50]. Herein, Pearson's correlation coefficient (r) was used to manifest the strength of the linear relationships between hydrochemical parameters (pH, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , and Eh) and the TDS in the groundwater samples, as shown in Figure 5. The statistical significance levels (p -values) were lower than 0.05. TDS and major ions, including Na^+ (0.67), Ca^{2+} (0.30), NO_3^- (0.53), and HCO_3^- (0.35), showed good and moderately positive correlations, suggesting significant contributions from these ions in the groundwater, representing the dissolution of salt rock and carbonate rock and indicating the occurrence of a water–rock interaction [51,52]. Meanwhile, it appears that anthropogenic contaminants have contaminated magnesium (e.g., fertilizer applications for magnesium), since there is a good and moderate correlation between Mg^{2+} with Cl^- and SO_4^{2-} ($0.9 > r > 0.5$).

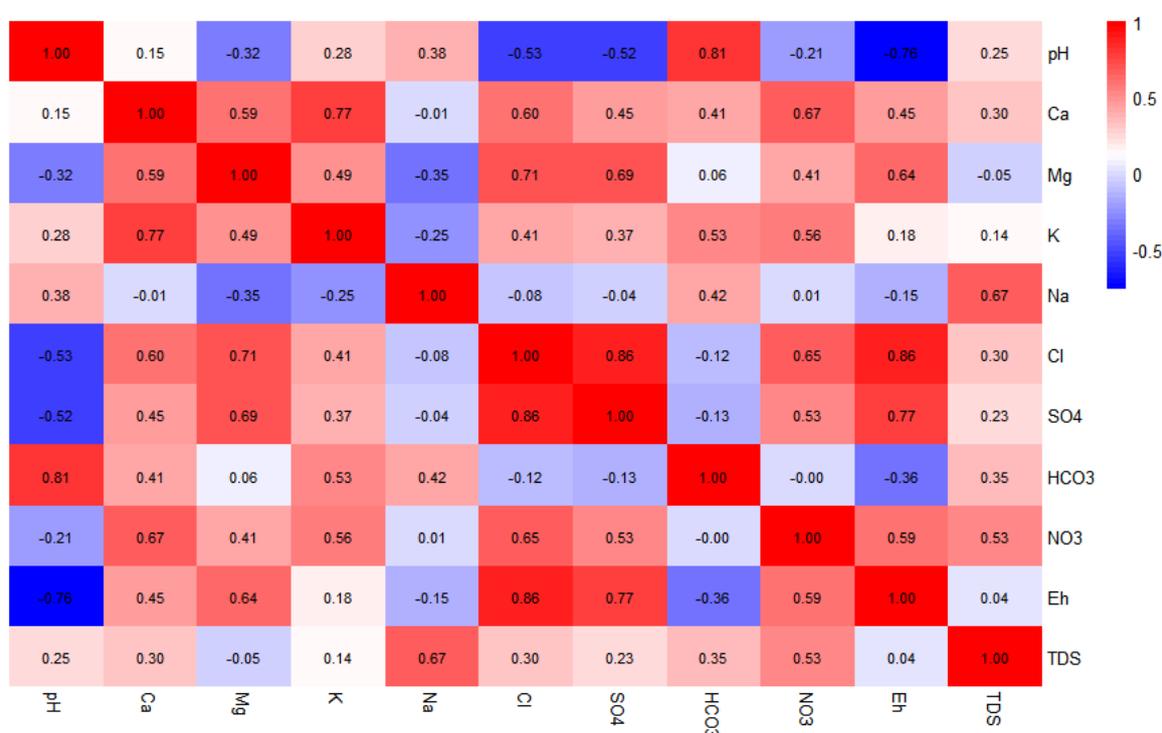


Figure 5. Correlation between major hydrochemical parameters of groundwater.

4. Conclusions

In this study, hydrochemistry and isotope analysis methods are used to investigate the recharge sources and hydrochemical processes of groundwater in Zhanjiang City. A total of 15 groundwater sites were sampled in March 2022. Hydrochemical plots such as Piper and Gibbs diagrams are used to analyze the controlling types and the hydrochemical processes of groundwater. In addition, Pearson's correlation coefficient (r) was used to manifest the strength of the linear relationships between hydrochemical parameters and TDS in the groundwater samples.

The isotopic composition of ^{18}O and D in the unconfined, middle, and deep confined groundwater indicate that the groundwater was mainly recharged by meteoric precipitation and was influenced by the effect of evaporation. The TDS of all groundwater samples was within the desirable limit of 1000 mg/L, indicating that the groundwater in this aquifer system is predominantly freshwater. The major cation and anion concentrations in unconfined and middle confined groundwater followed the order of $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, respectively, while the major ions

in the deep confined groundwater followed the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. The Piper diagram showed that the main chemical types in groundwater were $\text{Na}^+\text{Ca}-\text{HCO}_3$, which is a typical feature of recharge water sources. The results of the Gibbs diagrams revealed that water–rock interactions determine the hydrochemical characteristics of groundwater, followed by evaporation and precipitation. The correlation analysis further demonstrated that the dissolution of salt rock and carbonate rock are the dominant factors affecting the hydrochemical characteristics of groundwater, indicating the occurrence of a water–rock interaction.

This study highlights the effectiveness of hydrochemistry and isotope analysis methods for identifying the recharge area and recharge mode of groundwater, and it is significant for fully understanding groundwater hydrochemistry and scientifically managing and protecting groundwater.

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