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Hydrochemical Evolution and Quality Assessment of Groundwater in the Sanjiang Plain, China

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Abstract: Groundwater is subjected to contamination threats from human activities, such as agriculture, especially long-term farming in the Sanjiang Plain, China. Identifying the sources and distribution of pollution is essential for its reasonable prevention and control. In this study, we analysed the chemical characteristics of 389 samples at 60 shallow groundwater monitoring points from 2011 to 2015 in the Sanjiang Plain using traditional hydrochemical methods, water quality assessment, Pearson's correlation, and principal component analysis (PCA). Although groundwater type in this area was predominantly HCO_3-Ca·Mg, three forms of nitrogen pollution (ammonia, nitrate, and nitrite) were all detected in this area. The interaction of natural geochemical and anthropogenic factors during hydrochemical formation is confirmed by the high coefficients of variation and Gibbs plots of the main ions in the water. The overall shallow groundwater situation was described as good, with more than 40% and 90% of groundwater samples suitable for drinking and irrigation according to the quality assessment, respectively. The proportion of poor water quality in the wet season was higher than that in the dry season. NO_3-N and NH_3-N were identified as the major anthropogenic pollutants in the study area. Results from Pearson's correlation and principal component analysis shows two main pollutants fall into two chemical controlling factors together with natural chemical parameters, which implies that the migration and transformation of pollutants may have affected the overall hydrochemical characteristics of the regional groundwater. Therefore, findings from this paper can provide insight into the chemical evolution of groundwater in response to long-term agricultural activities and can help contribute to better management of groundwater resources and agricultural sustainable development.

Keywords: hydro-geo-chemistry; groundwater quality; nitrogen pollution; agricultural activities; Sanjiang Plain

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1. Introduction

The Sanjiang Plain has the largest area of natural marsh wetland distribution in China. Due to the special climatic conditions and geographical location, its soil has a remarkably high humus content, making it one of the four most precious native black soil belts globally [1]. Fertile land has also greatly promoted agricultural development in this area. Large wetlands areas have developed into farmlands since large-scale reclamation in the 1950s. In 2005, the arable land area was approximately 55,688 km^2 more than tripled from 17,134 km^2 in 1954 [2,3]. From 2010 to 2018, the arable land area increased by 3828.17 km^2. This area has become an important commodity grain base in China, with a per capita grain output three times higher than the national average [4]. However, long-term agricultural development has had a significant influence on the ecological environment. Specifically, the use of chemical fertilizers in agriculture has been increasing yearly, from less than 0.75 g/m^2 in the 1950s to more than 15 g/m^2 after 2000s [5]. The excessive accumulation of chemical fertilisers changed the soil's properties and seriously damages the health of the underground ecosystem [6,7].

Groundwater is an important carrier of underground environment materials and energy, and its chemical composition reflects the underground environment characteristics. Soil pollution caused by long-term agricultural activities indirectly generates signals on the groundwater chemical composition [8]. Sun et al. declare that the spatial variability of nitrate concentration in groundwater, total soil nitrogen, and shallow soil soluble nitrate-nitrogen have a moderately strong spatial autocorrelation, indicating that the vertical migration of pollutants is the primary cause of groundwater pollution [9]. Moreover, the relationship between nitrate concentration in groundwater and land use dominated by agriculture has been widely discussed. By comparing nitrate concentrations in shallow groundwater at different locations, Nolan et al. found that the most polluted wells were under farmland in the United States [10]. Yu et al. calculated that the average nitrogen concentration of rice fields and other agricultural land was about 5.1 mg/L and found that intensive agricultural land is the main cause of groundwater nitrogen pollution [11]. Therefore, high nitrogen concentrations in groundwater have been regarded as typical pollutants induced by agricultural activities. Based on the traceability analysis of stable isotopes of NO_3-δN, Cui et al. and Xu Chunying et al. verified that the main source of nitrate pollution in groundwater is chemical fertilisers [12,13]. In recent years, the rapid development of agriculture in the Sanjiang Plain has already caused groundwater pollution. The continuous decline of groundwater quality has led to water shortages in some farms and residential areas in the region [14]. Large-scale changes in land use are believed to cause nitrogen pollution in groundwater. Many studies have shown that high nitrate concentrations were found in shallow groundwater in this area [6,15,16]. However, groundwater is a dynamic mobile system, and nitrate is a highly migrated component in water. To identify and evaluate the impact of human activities such as agriculture on an underground environment, an in-depth multi-components analysis and discussion of groundwater chemical evolution over several years is necessary [17–19].

Hydrogeochemical methods are used to explore the evolution of groundwater quality and to analyse the origin of groundwater [20–22]. Generally, traditional hydrogeochemical methods can display an obvious overview of groundwater chemical characteristics but often fail to reflect the subtle and critical environmental and geological phenomena in local areas [23,24]. Besides, multivariate statistical methods are nowadays widely applied into groundwater chemistry research in Bangladesh and the Middle East, such as factor analysis, cluster analysis, and principal component analysis (PCA) [25–28]. Based on multivariate statistical methods, suitability of groundwater quality were assessed for irrigation and drinking, and the chemical origins of groundwater can be identified as well [29,30].

Therefore, based on multi-year monitoring data of shallow groundwater chemistry in the Sanjiang Plain, this study: (1) presents the chemical characteristics and evolution of shallow groundwater (within 60 m below the surface); (2) identifies pollution factors in the chemical composition of groundwater meant for drinking and irrigation; and (3) applies multivariate statistical methods to identify the agricultural impacts on groundwater chemistry throughout the study area. This research will provide more insight into the influence of agriculture on groundwater chemical evolution and provide a theoretical basis for the rational development, utilisation, and protection of groundwater resources in regional agricultural water resources.

2. Materials and Methods

2.1. Study Area

The study area falls in the flooded area of the Songhua River and Naoli River basins in the Sanjiang Plain, northeast China. It covers an area of 26,164 km^2, located between the latitudes 129°5731″ N and 133°5644″ N, and longitudes 46°637″ E to 47°4543″ E (Figure 1). With a temperate continental climate, the average annual precipitation and potential evaporation are 440–650 mm and 550–840 mm, respectively. The terrain gradually decreased from southwest to northeast. Black soil covers an area of 11,101 km^2, accounting for 72.8% of the total farmland area. The aquifer media distributed in the floodplain of the Songhua River, Naoli River, and its main tributaries comprise Holocene fine silt sand, fine sand, and gravel with a general thickness of 10–25 m. The types of groundwater mainly include floodplain pore water in valleys, terrace pore water-weakly confined water, and micro-pore fissure water in mountain terraces. The main recharge source of groundwater is the infiltration of atmospheric precipitation, and discharge from mainly lateral runoff, artificial exploitation, and evaporation. The groundwater depth along the Songhua River and the Naoli River basins is shallower than 2.5 m and gradually increases with the distance from the rivers, whereas the depth could increase to more than 10 m downstream of the Naoli River because of artificial exploitation. The agriculture irrigation area covers an area of 16,173 km^2, accounting for about 62% of the total area of the Sanjiang Plain.

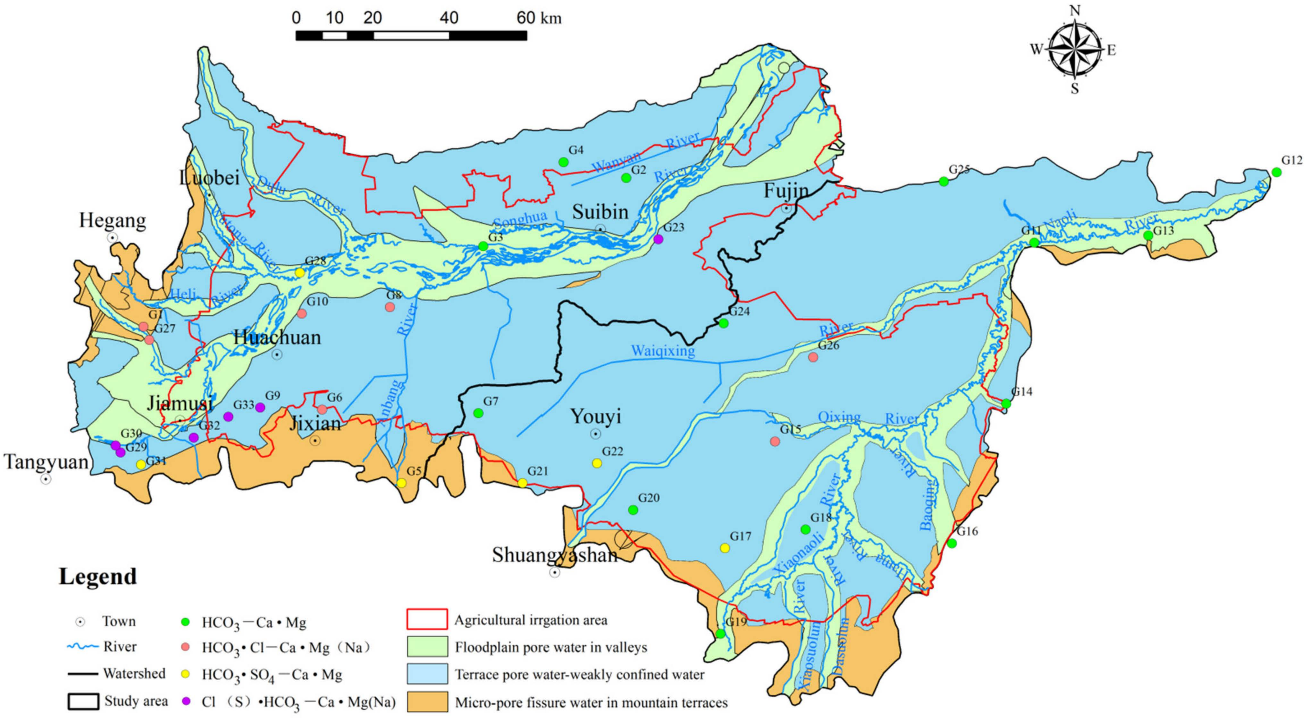

Figure 1. Study area and location of water sampling points.

2.2. Data Collection

Groundwater quality data were collected from the Heilongjiang Provincial Water Conservancy and Hydroelectric Power Investigation, Design, and Research Institute in China. However, considering the comparability of different source data, only the records of several regional shallow groundwater investigations were used in this study, which included: (1) 33 samples in May 2011 (wet season, 2011-W); (2) 33 samples in October 2011 (dry season, 2011-D); (3) 52 samples in May 2012 (wet season, 2012-W); (4) 52 samples in October 2012 (dry season, 2012-D); (5) 51 samples in May 2013 (wet season, 2013-W); (6) 51 samples in October 2013 (dry season, 2013-D); (7) 57 samples in May 2015 (wet season, 2015-W); and (8) 60 samples in October 2015 (dry season, 2015-D). In summary, 389 samples from shallow groundwater from 2011–2015 were included.

These samples were analysed with water chemical analysis. Among the water index, general indicators (pH, EC, total dissolved solids (TDS), and total hardness (TH); concentrations of major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $HCO_3{}^-$, $CO_3{}^{2-}$), and regional enriched metal elements (Fe, Mn) were used to analyse the evolution of regional groundwater characteristics. In addition, the nitrogen pollution index (including NH_3-N,

NO_3-N, and NO_2-N) was used to provide general information of groundwater quality contaminated by agricultural activities.

2.3. Traditional Hydrochemical Analysis

Traditional hydrogeochemical methods are widely applied to explore groundwater quality evolution and groundwater recharge sources [22]. First, Piper Trilinear diagram of major cations and anions were drawn to analyse the chemical components of groundwater samples. A Gibbs plot was then employed to identify the sources of water compositions. It can directly reflect the dominant factors, such as precipitation, rock weathering, or evaporation, and provide a qualitative reference for their impacts on water chemistry [31].

2.4. Water Quality Index

The water quality index (WQI) was computed according to drinking requirements to identify the pollution components in groundwater and its suitability to drinking purposes [32]. Five steps were involved in the WQI calculation: (i) according to the World Health Organization Water Quality Standard (WHO2011), 11 available parameters including K^+, Na^+, TH, Cl^-, $SO4^{2-}$, TDS, pH, NO_3-N, NO_2-N, Fe, and Mn were selected for calculation; (ii) each parameter was given a weight (w_i) in terms of its relative importance in the overall water quality (Table 1); (iii) the relative weights (W_i) of each parameter involved were calculated based on (1); (iv) quality rating scale (q_i) for each parameter was calculated following (2); (v) WQI is the weighted sum of all the parameters' quality rating scale (3). The computed WQI values were categorised into five classes: excellent, good, poor, very poor, and unsuitable for drinking.

$$W_i = w_i / \sum_{i=1}^{n} w_i \quad (1)$$

$$q_i = (C_i/S_i) * 100 \quad (2)$$

$$WQI = \sum W_i \cdot q_i \quad (3)$$

where W_i is the relative weight, w_i is the weight of each parameter, n is the number of parameters, q_i is the quality rating scale, C_i is the concentration of each chemical parameter in each sample in mg/L, and S_i is the World Health Organization standard for each chemical parameter in mg/L according to the guidelines of the WHO (2011).

Table 1. The relative chemical weight of the physicochemical parameters (all values are in mg/L, except for pH).

Chemical Parameters	WHO Standards (2011)	Weight (w_i)	Relative Weight (W_i)
K	200	2	0.048
Na	200	2	0.048
TH (as $CaCO_3$)	100–200	2	0.048
Cl	250	3	0.071
SO_4	250	4	0.095
TDS	500	5	0.119
pH (on scale)	6.5–8.5	4	0.095
NO_3	50	5	0.119
NO_2	3	5	0.119
Mn	0.1	5	0.119
Fe	0.3	5	0.119
Total		42	1

2.5. Risk Assessment for Irrigation

With the expansion of farming areas, groundwater exploitation has become a primary way of agricultural irrigation due to its availability and low cost. However, poor quality irrigation water adversely affects farmland soil. Therefore, to evaluate the hazard risk of groundwater used to irrigate black soil, the following irrigational quality parameters were estimated: percent sodium (%Na) (4), sodium adsorption ratio (SAR) [33] (5), and the permeability index (PI) (6) were used, which were calculated as follows (all ionic concentrations are in meq/L):

$$\%Na = \left(\frac{Na^{+} + K^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \right) \times 100 \quad (4)$$

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad (5)$$

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+}} \times 100 \quad (6)$$

The salinity hazard was determined by the total concentration of soluble salts in water. It was classified into four levels: low (EC < 250 µs/cm), medium (250–750 µs/cm), high (750–2250 µs/cm), and very high (2250–5000 µs/cm) [34]. Sodium hazard is expressed in terms of the percent sodium (Na%) and sodium adsorption ratio (SAR). Water was classified as low (<10), medium (10–18), high (18–26), and very high (>26) sodium hazards based on the sodium adsorption ratio [34,35]. In addition, the classification of water-based on percent sodium was classified as excellent (<20%), good (20–40%), permissible (40–60%), doubtful (60–80%), and unsuitable (>80%) [36]. Lastly, water was classified based on PI into three classes: class I (>75%), class II (25–75%), and class III (<25%). (WHO1989)

2.6. Statistical Analysis

Descriptive statistics provide a general view of the hydrochemical characteristics [37]. In addition, interrelationships in a set of chemical variables were determined using factor analysis. The underlying but unobservable or latent processes which the raw dataset cannot directly reveal can be more clearly interpreted by factor analysis [38]. In this study, the R-mode was used for factor analysis to identify the hydrochemical controlling factors involved. Hypothesis testing showed that TDS was significantly associated with major ions ($p < 0.01$), and ammonia nitrogen was significantly associated with heavy metals. The dimensionality of the parameters was then reduced by PCA to reveal the association patterns between the hydrochemical variables. The measurements of pH and the concentrations of TDS, TH, and the major ions in the groundwater were analysed to identify the main factors controlling the chemical components of groundwater [39,40].

3. Results and Discussion

3.1. Chemical Characteristics of Groundwater

3.1.1. General Hydrochemistry

The statistical analysis of groundwater hydrochemical parameters helps understand water chemical composition's enrichment and change law. Table 2 shows the maximum, minimum, average, variance, and coefficient of variation for each parameter. The results indicate that 98.47% of the samples were associated with neutral water (pH 6.2–8.3) except for individual extreme points of pH. As an important indicator of water palatability, TDS is between 109 and 2950 mg/L, and 51.57% of the samples exceeded the acceptable limit for drinking (500 mg/L), indicating about half of the water samples was distorted in taste due to high TDS. The TH of the groundwater reflects the lithological formation of the aquifer. Generally, water is classified based on TH value as soft water (<150 mg/L) and hard water (>150 mg/L). Among the samples, 76.68% were hard water, and 23.32% were soft water. The TH value was between 40–2430 mg/L, with an average of 284 mg/L. According to the statistical analysis, the cation abundance in the water samples was $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$. The calcium and magnesium ions concentrations ranged from 9.94–579 mg/L and 2.31–238 mg/L, with average values of 74.62 mg/L and

23.79 mg/L, respectively. A total of 2.16% of the sample's calcium ion concentration was relatively high, exceeding the World Health Organization guideline value (200 mg/L). The sodium and potassium ions concentrations ranged from 4.88–179 mg/L and 0.29–218 mg/L, with the average values being 35.78 mg/L and 5.89 mg/L, respectively. The order of the anion concentration was $HCO_3^- > Cl^- > SO_4^{2-}$, the observed bicarbonate and chlorine concentrations ranged from 22.8–1430 and 0.19–1570 mg/L, and the average values were 171.89 and 69.70 mg/L, respectively. Nitrogen pollution is mainly caused by ammonia nitrogen, nitrate, and nitrite pollution. The NH_3-N, NO_3-N, and NO_2-N concentrations in groundwater samples were 0–4.51, 0–148, and 0–4.2 mg/L, with average values of 0.36, 24.03, and 0.04 mg/L, respectively (Table 2).

Table 2. Maximum, minimum and average chemical composition and variance of groundwater samples (all values are in mg/L, except for pH and EC).

	max	min	ave	sd	cv
pH	8.3	6.2	6.83	0.31	5%
EC (μs/cm)	4570	171	920	643	70%
TDS	2950	109	576	370	64%
Na	179	4.88	35.78	26.51	74%
K	218	0.29	5.89	14.76	250%
Ca	579	9.94	74.62	67	90%
Mg	238	2.31	23.79	21.41	90%
HCO_3	1430	22.8	171.89	113.45	66%
SO_4	468	0.21	65.93	67.74	103%
Cl	1570	0.19	69.7	126.51	181%
TH	2430	40	284	248	87%
NO_3-N	148	0	24.03	30.78	128%
NH_3-N	4.51	0	0.36	0.52	143%
NO_2-N	4.2	0	0.04	0.26	603%
Fe	79.8	0	2.46	8.26	336%
Mn	10.3	0	0.62	1.28	205%

The degree of dispersion of the samples was a necessary reference for classification. The coefficients of variation of K, NO_2-N, Mn, and Fe were >200%. The wetland part of the Sanjiang Plain experiences slow sedimentation leading to the accumulation of iron in the underlying groundwater and sediments. In addition, the complexation of natural organic compounds can prevent or delay the precipitation of oxyhydroxides. Therefore, the swamp system in the Sanjiang Plain is considered to play a vital role in species control and iron output [41]. The coefficients of variation of Cl, SO_4^-, NO_3-N, and NH_3-N were >100%, indicating that the groundwater may have been affected by human activities. The coefficients of variation of Na^+, TH, TDS, Ca^{2+}, Mg^{2+}, HCO_3^-, and EC are >60%, and the index values had certain discrete distribution characteristics, which may be indicators that exceed the standard.

3.1.2. Hydrochemical Facies

Groundwater hydrochemical facies shows the chemical composition categories of groundwater, and reflects the variability of hydrochemical parameters in response to chemical processes during transport in the lithologic framework [42,43].

Piper diagram can provide a comprehensive view of the hydrochemical phases and types of groundwater [44–46]. According to the Piper diagram (Figure 2), the cation plot shows that most samples are concentrated in Zone A, indicating that the groundwater is mainly of the "calcium" type. About a quarter of the samples fall in the "no dominant" type (zone B) and "sodium" type (zone D) due to the increasing proportion of sodium in water. In the anion plot, sample points are more dispersedly distributed in zones E and B, suggesting the dominance of bicarbonate or mixed anions. The central diamond field shows the overall features of groundwater chemistry [45]. As shown in Figure 2, almost all groundwater samples are plotted in zones I and IV, illustrating that HCO_3-Ca·Mg and Cl· SO_4-Ca·Mg were the dominant water types. Only a few samples occurred in zones II and III. Similar results were also reported by Lu et al. [47] for the Abujiao River Basin, which is part of the Sanjiang Plain. Additionally, samples in zone I were mainly characterised by freshwater (TDS < 1000 mg/L), and samples in zone 4 (Cl-Ca type) and near zone 5 were all high in TDS.

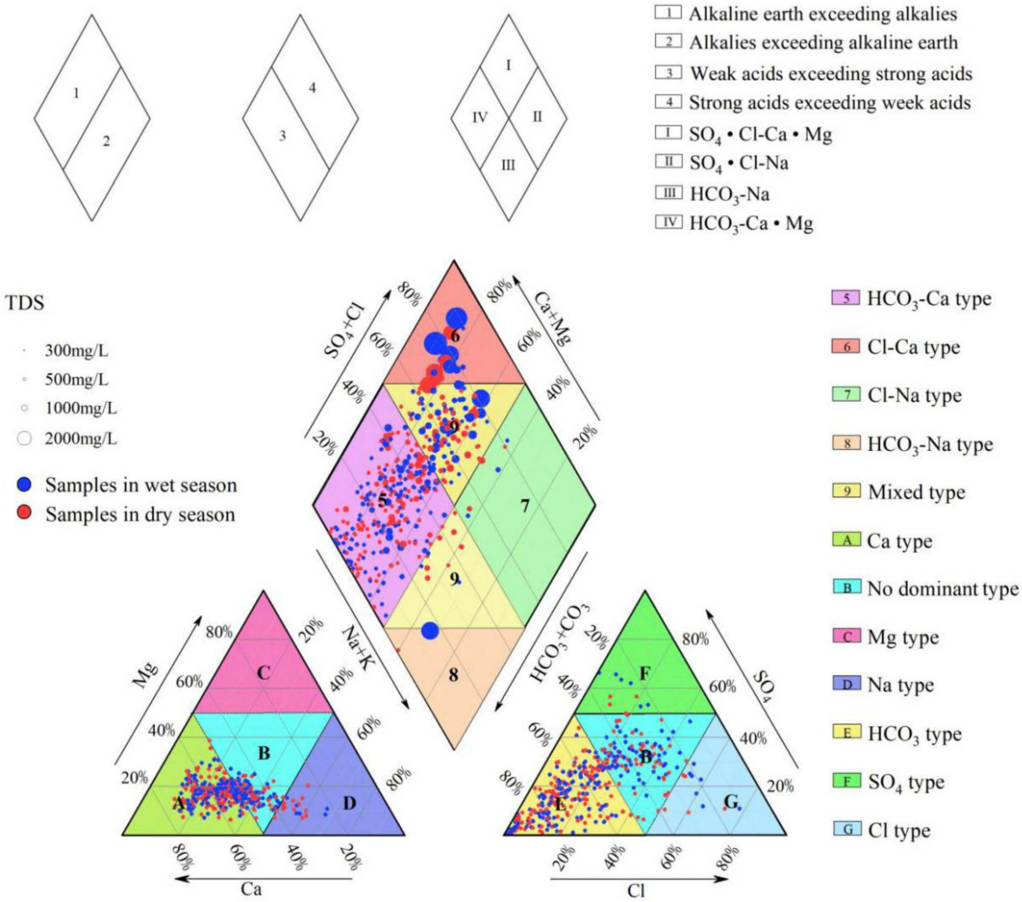

Figure 2. Piper diagram for the groundwater.

According to the distribution of varied hydrochemical facies over the region (Figure 1), we observed that the pore phreatic water and weak confined water along the river valley and terrace were mostly of HCO_3-Ca·Mg type. On the contrary, the chemical type of micro-pore fissure phreatic water in the mountain front of the evaluation area was mostly of HCO_3·SO_4-Ca·Mg type, and gradually changed into HCO_3·Cl-Ca·Mg type in the lower reaches. A high density of Cl·HCO_3 or Cl·SO_4 water mainly appeared in the vicinity of Jiamusi, and the proportion of Na among the cations was also significantly increased.

3.1.3. Mechanisms Controlling Groundwater Chemistry

The mechanisms governing the major dissolved chemical ions constituents were summarized into three dominant processes of precipitation, rock weathering, and evaporation (Gibbs, 1970). Two diagrams of the weight ratios of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ (x-axis) against TDS (y-axis) were presented by Gibbs to identify the functional sources of dissolved chemical compositions. The Gibbs diagram (Gibbs, 1970) was primordially used to represent the mechanism controlling the evolution of the world's surface water, and it has been widely used in groundwater research.

According to the Gibbs diagram (Figure 3), 99.13% of the sampling points in the relationship chart between $Na^+/(Na^+ + Ca^{2+})$ and TDS fell within the rock weathering zone, while 96.07% was observed for $Cl^-/(Cl^- + HCO_3^-)$. This indicates that the cation content is mainly affected by rock weathering, and anion content is controlled by rock weathering and evaporation. Moreover, the "bicarbonate type" samples were mainly plotted in the rock dominance zone, suggesting that rock weathering and leaching are the major mechanisms controlling groundwater chemistry in these areas [48]. The other types of distributions all showed a slight increasing trend towards the evaporative dominance band. Some samples still fell outside the Gibbs field, which may have been affected by anthropogenic sources [49]. However, anthropogenic activities, especially irrigation, can also impact evaporation [50] since large-scale irrigation increases the groundwater level. Our results indicate that rock weathering is the most important factor influencing groundwater evolution; evaporation and anthropogenic activities may contribute to water chemistry.

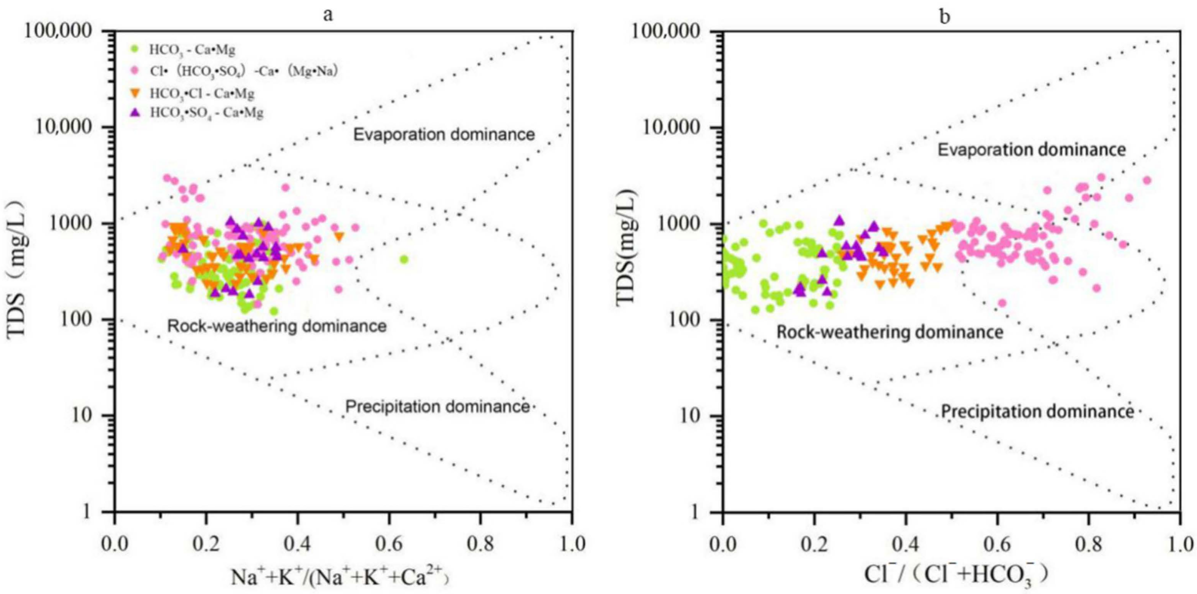

Figure 3. Gibbs diagrams showing the mechanism controlling groundwater chemistry of (**a**) TDS vs. cations and (**b**) TDS vs. anions.

3.2. Groundwater Quality Assessment

3.2.1. Groundwater Quality for Drinking

Water Quality Assessment Index (WQI) is an aggregated communication tool for monitoring water quality [51], developed to summarise a huge amount of water quality data in a format that is easy to present and understand, with less information than the original data. In this study, WQI was employed to evaluate groundwater quality status for drinking water purposes. According to the WHO (2011) standard, the distribution weight (W_i) and relative weight (w_i) of each parameter are listed in Table 1, and the calculated WQI values of samples in this area ranges from 5.65–3268.19. The distinguished classifications based on WQI scores are: (I) <50, excellent water; (II) 50–100, good water; (III) 100–200, poor water; (IV) 200–300, very poor water; and (V) >300, unfit for drinking water. As shown in Figure 4a, the proportion of poor-quality water in the wet season was higher than that in the dry season, and the water quality deteriorated first and then improved. The over-standard ratio was 27.03% in 2011, increasing to 59.65% in 2013 and dropping to 23.73% in 2015. The proportion of available drinking water in each period was higher than 40%, and the proportion of poor-quality water was higher than 23.73%.

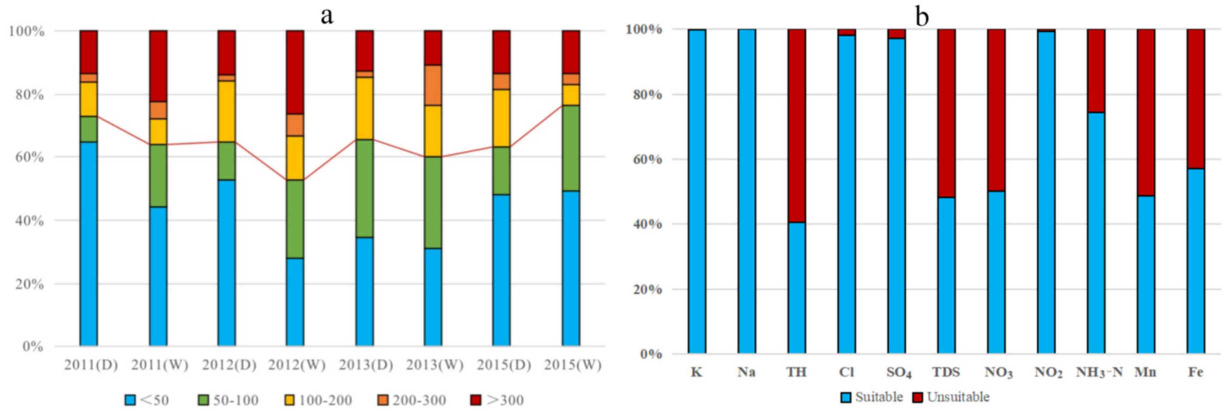

Figure 4. Grades histogram of groundwater samples for drinking purposes in seasons (**a**) and parameters (**b**).

Furthermore, statistics of each chemical parameter compared to those in the WHO standards are presented in Figure 4b. Five chemical parameters, distinguished by more than 40% of the samples, were above the recommended WHO limit in the following order: TH, TDS, NO_3-, Mn, and Fe. Hardness in water is mainly caused by magnesium and calcium [52], the main cations in the groundwater of this region. Thus, the TH and TDS of more than 50% of the water samples exceeded those of the WHO's drinking water standards. This high TH and TDS can be mainly attributed to the dissolution of soluble salts and minerals, and evaporation because most of the study area is located downstream of the watershed, as well as wastewater infiltration. NO_3- is one of the main pollutants in groundwater in the world's cultural regions [53] In the study area, the nitrate concentration of 49.76% of water samples were beyond the permissible limits of WHO standards, and are associated increased with soil cover nitrate fertilisers from agricultural practices. In addition, NO_3-N, NO_2-N, and NH_3-N in water can be interconverted under certain favourable conditions [6]. Although only 0.72% water samples had NO_2^- content above the permissible limit, the over-limit ratio of NH_3-N is up to 25.48%, according to the Chinese drinking water standard. However, groundwater's Fe concentrations in this area reached high levels because of their geochemical nature [54]. Therefore, NO_3-N and NH_3-N were identified as the major anthropogenic pollutants in the study area.

3.2.2. Groundwater Quality for Irrigation

In this basin, groundwater is mainly extracted for drinking and irrigation, while water quality requirements vary for different purposes. To assess the suitability of groundwater for irrigation purposes, three indices relevant to sodium were used in the study: %Na, SAR, and PI.

The %Na values of the study area varied from 9.78–67.72%, with a mean value of 29.89%. In terms of the classification suggested by Wilcox (1955), 94.69% of the samples indicated %Na values in good and permissible limits, whereas 3.86% and 1.45% of samples were doubtful and unsuitable for irrigation purposes respectively (Figure 5a). SAR is the main factors that determine the suitability of water for agricultural purposes. Naseh et al. evaluated the agricultural water suitability of the Ghaen Plain according to SAR. [55]. As shown in Figure 5b, approximately 97.10% of the samples with low SAR pose almost no risk of exchangeable sodium and are of excellent water quality for irrigation. Only 2.90% of samples of high and very high sodium water (in C4S1 and C5S1) were regarded as unfavourable, as they contained detrimental levels of exchangeable sodium in soils. Figure 5c presents the PI value distribution of the samples that ranges from 13.42–112.17, with an average of 52.87. According to the PI value, approximately 69.31% of the groundwater samples belong to Category I, indicating that the water was good or moderate for irrigation purposes. Of the groundwater samples, 26.73% belonged to Type II (barely suitable), and the remaining (3.96%) belonged to Type III (not suitable for irrigation). Therefore, assessment of all the indices shows that most groundwater in this area is safe for irrigation and pose no risk of soil damage. By contrast, the proportions in each quality category assessment varied assessment with different indices because these indices considered different reactions of the sodium in water with soil, according to the equations of each index.

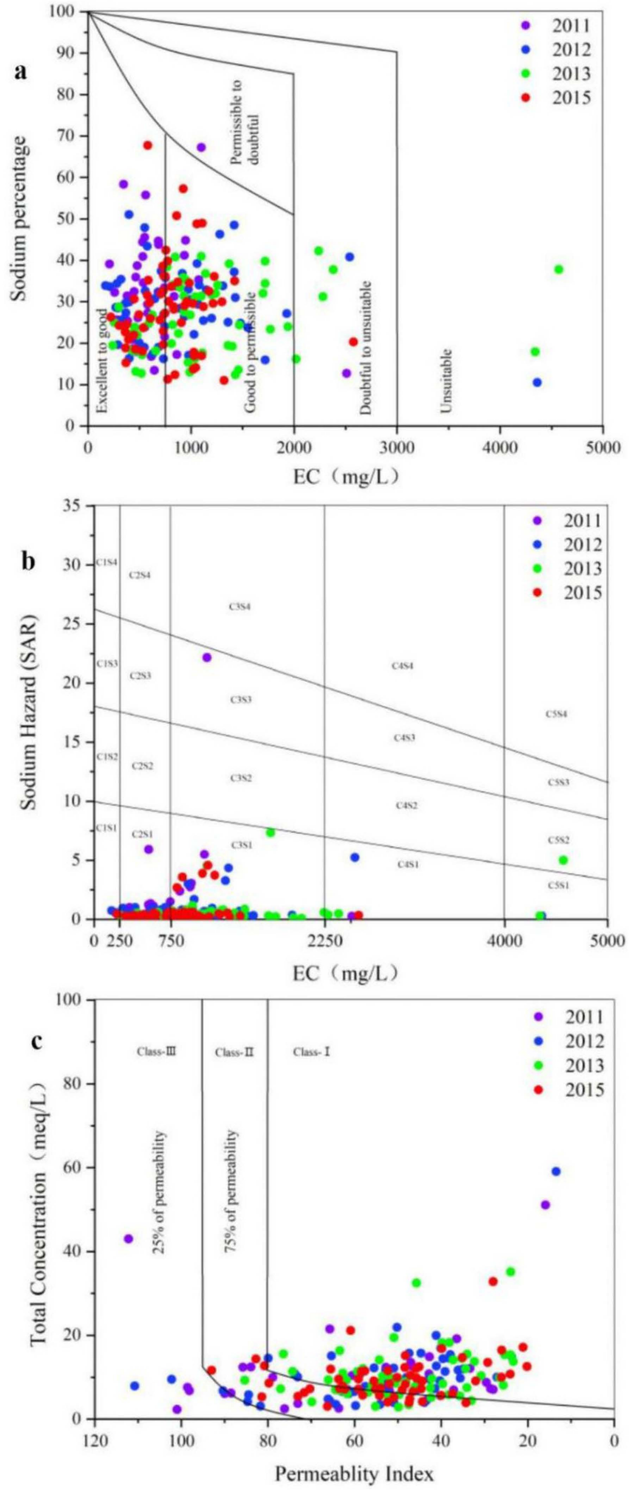

Figure 5. Irrigations hazards classifications by sodium percentage (**a**), sodium adsorption ratio, SAR (**b**), and permeability index, PI (**c**).

3.3. Statistical Analysis of Hydrochemistry

3.3.1. Ion Correlation Matrix Analysis

Pearson's correlation expressed the relationships among the different parameters [56]. According to the correlation coefficient (R), the relevance degree can be divided into three levels: strong (R > 0.7), moderate (0.7 > R > 0.3), and weak (R < 0.3) [57].

Figure 6 shows the correlation curves between all pairs of the 15 parameters. In the study area, TDS exhibited a strong positive relationship with TH (R = 0.93), Ca^{2+} (R = 0.92), Mg^{2+} (R = 0.84), Cl^{-} (R = 0.77), and Na^{+} (R = 0.71), which is a common understanding of natural geochemistry of groundwater in alluvial plains. Regarding nitrogen as a typical agricultural pollutant, there was no strong correlation among the three forms of nitrogen (NO_3-N, NO_2-N, and NH_3-N), whereas the NO_3-N concentration in groundwater was proportional to TDS. The moderate positive correlation between NH_3-N and Fe and Mn suggests that reduction conditions are one of the reasons for the high NH_3-N concentration. The weak correlation between NO_2-N and other parameters was due to its low concentration.

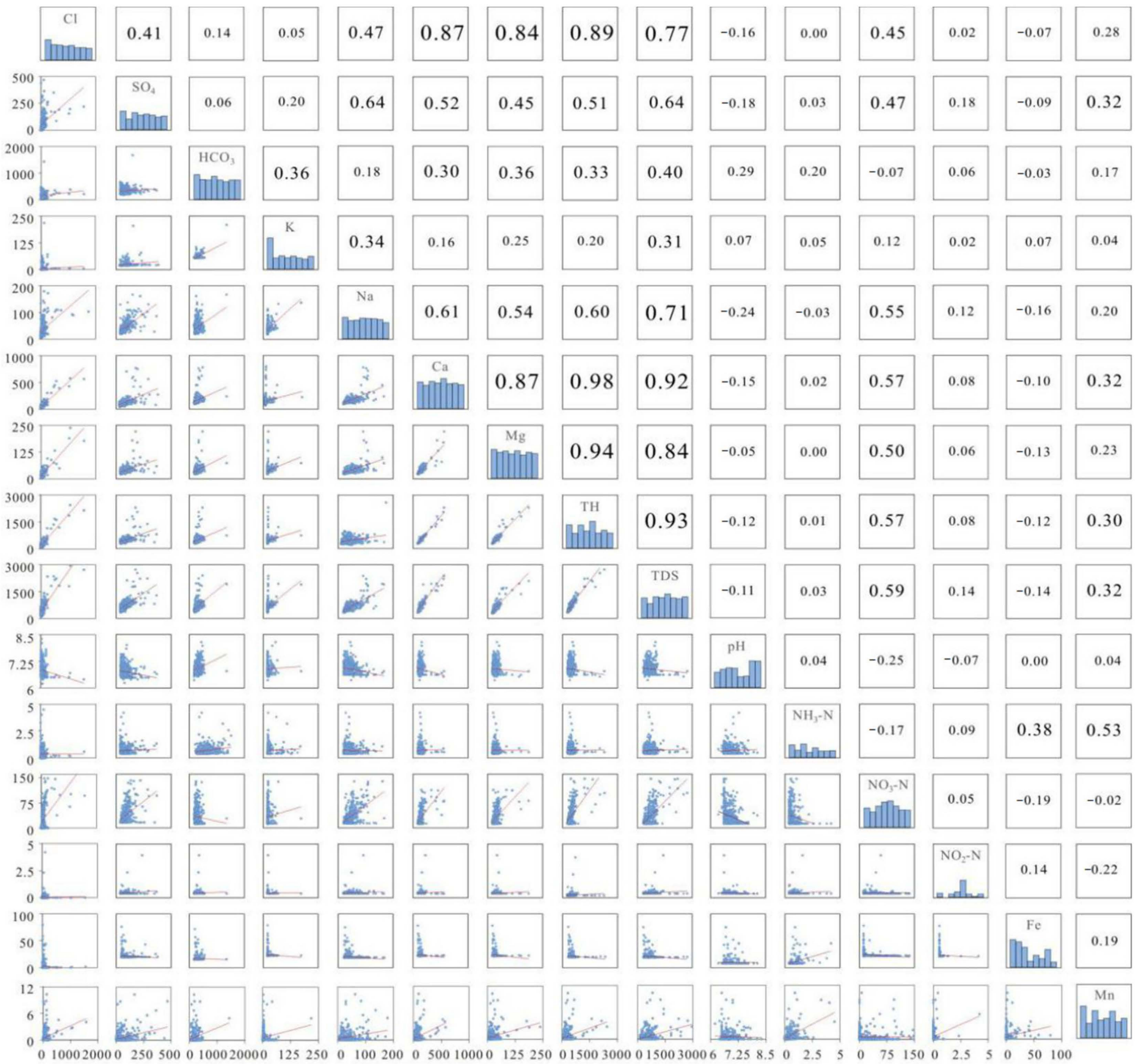

Figure 6. Relationships between different chemical parameters and histogram of each parameter's annual average change.

The annual average histogram of each parameter is shown in Figure 5. During 2011–2015, TDS and the concentration of its closely related ions fluctuated in a certain value range, whereas NO_3-N and NO_2-N concentration initially increased and then decreased after implementing the "three reductions" in agriculture since 2013 [58]. However, NH_3-N did not show an obvious decrease during this period.

3.3.2. Principal Component Analysis

PCA was used to track the contribution of natural and human factors to the groundwater hydrochemistry components. Twenty-five indicators were analyzed by PCA for dimensionality reduction in the southern Tehran aquifer [59]. For the Sanjiang Plain, four principal components (PCs) with eigenvalues above 1 were retained, which explained 71.75% of the total variance (Figure 7). PC1 with the greatest variance (40.66%) decides the hydrochemical characteristics and is affected by positive loadings of TDS (0.964), TH (0.961), Ca^{2+} (0.948), Mg^{2+} (0.902), Cl^- (0.845), Na^+ (0.748), SO_4^{2-} (0.668), and NO_3-N (0.645) (Table 3). The loadings on PC1 indicate that multiple processes, including carbonate weathering, anthropogenic factors, and evaporite dissolution, may be the main sources of these ions [60]. PC2 accounted for 12.90% of the total variance, with strong loadings for NH_3-N (0.811), Mn (0.673), and Fe (0.528). The positive loadings of these three parameters imply an anoxic and reducing environment and the influence of human activities because of the inclusion of NH_3-N. PC3 accounted for 10.09% of the total variance and mainly comprised pH (0.644) and HCO_3^- (0.640). The loadings on PC3 further indicate that mineral weathering affects water chemistry. PC4 explained 8.10% of the variance and had positive NO_2-N (0.529) and K^+ (0.52) loadings. The high positive loading of NO_2-N indicates the contribution of anthropogenic factors on water chemistry.

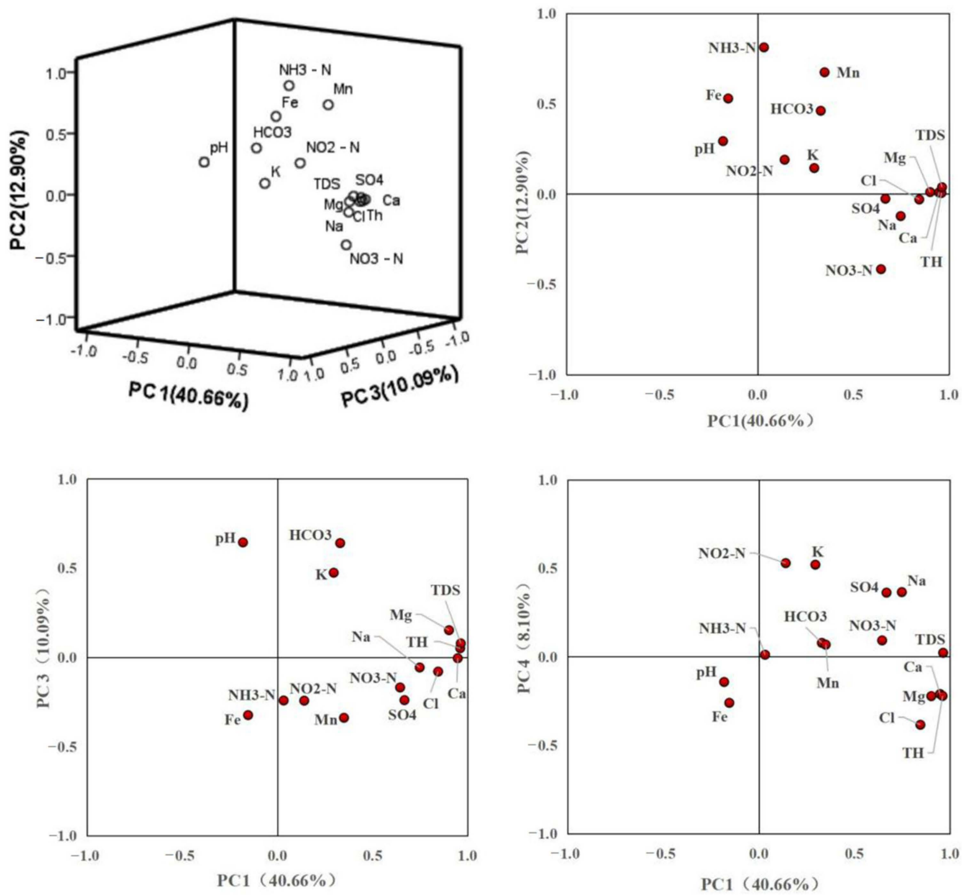

Figure 7. Principal components load diagrams.

Table 3. Element matrix of PCA.

	PC1	PC2	PC3	PC4
Cl	0.845	−0.031	−0.08	−0.385
SO_4	0.668	−0.027	−0.24	0.362
HCO_3	0.33	0.46	0.64	0.078
K	0.296	0.143	0.474	0.52
Na	0.748	−0.123	−0.057	0.365
Ca	0.948	0.008	−0.005	−0.211
Mg	0.902	0.01	0.152	−0.223
TH	0.961	0.005	0.051	−0.222
TDS	0.964	0.037	0.078	0.022
pH	−0.181	0.292	0.644	−0.143
NH_3-N	0.033	0.811	−0.242	0.011
NO_3-N	0.645	−0.417	−0.169	0.092
NO_2-N	0.141	0.189	−0.243	0.529
Fe	−0.154	0.528	−0.324	−0.261
Mn	0.35	0.673	−0.339	0.068

4. Conclusions

The Sanjiang Plain plays a pivotal role in food production in China. However, large-scale reclamation and agricultural development, human activities, and excessive fertiliser application have led to the deterioration of the groundwater environment in the Sanjiang Plain, and the nitrogen content of the groundwater also shows complex changes. Therefore, chemical investigation of the groundwater was carried out to rationalise the development of groundwater resource utilisation and protection. The results are as follows:

(1) In the study area, the cation abundance in shallow groundwater was $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$, and the order of the anion concentration was $HCO_3^{-} > Cl^{-} > SO_4^{2-}$. Three forms of nitrogen pollution, ammonia, nitrate, and nitrite were detected in this area. In addition, the coefficients of variation of Cl, SO_4, NO_3-N, and NH_3-N were higher than 1, indicating that the groundwater may have been affected by human activities.

(2) There are four types of hydrogeochemical groundwater, and the main HCO_3-type water accounted for 63.09% of the groundwater samples. The hydrochemical type, indicated by the Piper diagram, transits from HCO_3–Ca·Mg or $HCO_3 \cdot SO_4$–Ca·Mg to $HCO_3 \cdot$Cl–Ca·Mg type along the flow path in nature, but some abnormal points should be the result of human interference.

(3) Water assessment by WQI and irrigation index showed that the proportion of available drinking water in each period was higher than 40%, and more than 90% of the groundwater in the study area was suitable for irrigation. In addition, nitrogen was identified as a typical anthropogenic pollutant in this area. Comparing the seasonal and annual variations in groundwater quality, the proportion of poor water quality in the wet season was higher than that in the dry season, and the water quality deteriorated first, but improved during the final year of the 2011–2015 period.

(4) Although groundwater chemistry is still of rock dominance, it is increasingly influenced by agricultural activities. Three of the four principal components extracted by PCA are relevant to anthropogenic factors, explaining 71.75% of the variance in groundwater chemistry, and the first two PCs show the interaction of both natural and anthropogenic factors. The typical pollutants of the three nitrogen forms (NO_3, NH_3, and NO_2) were determined by PC1, PC2, and PC4, respectively.

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