sustainability

MDPI

Article

Exploring the Hydrochemical Characteristics and Controlling Processes of Groundwater in Agricultural Lower Reaches of a Typical Arid Watershed on Tibetan Plateau

Zhen Zhao [1,2,3], Gongxi Liu [4,5], Guangxiong Qin [1,2,3,*], Huijuan Chen [1,2,3], Huizhu Chen [6], Wenxu Hu [4,7], Shaokang Yang [1,2,3], Jie Wang [4,8], Yuqing Zhang [4,8], Dongyang Zhao [1,2,3], Yu Liu [9] and Yong Xiao [4,7,8,*]

1 Bureau of Qinghai Environmental Geological Prospecting, Xi'ning 810007, China
2 Key Lab of Geo-Environment of Qinghai Province, Xi'ning 810007, China
3 Qinghai 906 Engineering Survey and Design Institute Co., Ltd., Xi'ning 810007, China
4 Faculty of Geosciences and Engineering, Southwest Jiaotong University, Chengdu 611756, China
5 Geothermal and Geological Party, Geological Mineral Exploration and Development Bureau of Tibet Autonomous Region, Lhasa 850000, China
6 School of International Studies, Chengdu College of Arts and Sciences, Chengdu 610401, China
7 MOE Key Laboratory of Groundwater Circulation and Environmental Evolution, China University of Geosciences (Beijing), Beijing 100083, China
8 Sichuan Province Engineering Technology Research Center of Ecological Mitigation of Geohazards in Tibet Plateau Transportation Corridors, Chengdu 611756, China
9 Xiamen Institute of Environmental Science, Xiamen 361006, China
* Correspondence: qin_guangxiong@163.com (G.Q.); xiaoyong@swjtu.edu.cn (Y.X.)

Abstract: Groundwater is crucial for domestic, agricultural, and ecological uses, particularly in the lower reaches of arid basins, where its quality often limits availability. A total of 26 phreatic groundwater samples were collected from a typical endorheic watershed on the Tibetan Plateau to assess the hydrochemical characteristics of phreatic groundwater in the lower reaches of arid inland watersheds. The hydrochemical characteristics, quality, and formation mechanisms of groundwater were analyzed using the Entropy-Weight Water Quality Index (EWQI), irrigation water quality indexes (such as sodium adsorption ratio, soluble sodium percentage, and permeability index), hydrochemical diagrams, and correlation analysis. The findings indicate that phreatic groundwater in the lower reaches is slightly alkaline, with a substantial TDS variation from 252.58 to 1810.41 mg/L. Groundwater is predominantly characterized by fresh hydrochemical facies of HCO_3-Ca and HCO_3-Na types, with a few saline Cl-Na types present. The concentrations of NO_3^-, NO_2^- and NH_4^+, in groundwater range from 0.32 to 100.00 mg/L, 0.00 to 0.48 mg/L, and 0.00 to 0.20 mg/L, respectively, and 3.59%, 26.92%, and 7.69% of the samples exceeding the permissible drinking limits recommended by Chinese guideline and World Health Organization. Groundwater is classified as fresh at 80.8% of sampling sites and brackish at 19.2%. Approximately 96.2% of the sampled groundwaters is rated as excellent to medium quality according to EWQI assessments, suitable for domestic use, while 3.8% is of extremely poor quality and should be avoided for direct consumption. Groundwater from all sampling sites is suitable for agricultural irrigation and does not pose permeability hazards to the soil. Most groundwaters are suitable for long-term irrigation in terms of sodium hazards, with only 3.8% and 7.7% of samples falling into the "Permissible to Doubtful" and "Doubtful to Unsuitable" categories, respectively. Salinity poses the primary threat in long-term irrigation, with 38.5%, 53.8%, and 7.7% of sampled groundwaters exhibiting moderate, high, and very high salinity risks, respectively. Groundwater chemistry is primarily governed by water-rock interaction and evaporation, with additional impacts from agricultural inputs of nitrogen contaminants and chemicals. Agricultural practices contribute to elevated groundwater salinity in the study area, while natural evaporation

check for updates

Academic Editor: Andrea G. Capodaglio

Received: 29 December 2024
Revised: 25 February 2025
Accepted: 27 February 2025
Published: 28 February 2025

Citation: Zhao, Z.; Liu, G.; Qin, G.; Chen, H.; Chen, H.; Hu, W.; Yang, S.; Wang, J.; Zhang, Y.; Zhao, D.; et al. Exploring the Hydrochemical Characteristics and Controlling Processes of Groundwater in Agricultural Lower Reaches of a Typical Arid Watershed on Tibetan Plateau. *Sustainability* **2025**, *17*, 2117. https://doi.org/10.3390/su17052117

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

drives salinity accumulation in the lower parts. In managing and utilizing groundwater resources in the study area and similar arid regions globally, attention should be paid to salinity caused by agricultural activities and natural evaporation, as well as nitrogen pollution from farming.

Keywords: hydrochemistry; groundwater salinity; nitrite contamination; agricultural pollution; arid basin

1. Introduction

Water resources are essential for global agriculture, industry, and human life, and play a crucial role in sustaining ecosystem balance and biodiversity [1–3]. However, arid and semiarid regions, such the Qaidam Basin on Tibetan Plateau, face significant water scarcity, due to limited precipitation and surface water availability, which is exacerbated by unique climatic and environmental constraints [4]. In these regions, groundwater emerges as the primary water source for human society development and eco-environment sustenance [5,6]. The increasing water demand driven by rapid industrial and agricultural growth is placing unprecedented pressure on groundwater resources in arid and semiarid areas [2,7]. Groundwater's solvent properties make it a key transporter of chemicals, and its hydrochemical composition determines its suitability for drinking, domestic use, and irrigation [8]. But, groundwater quality in these regions is increasingly threatened by multiple factors, including human activities and climate change. For example, studies in Egypt, Bangladesh, China, and Italy have highlighted the degradation of groundwater quality due to pollution and overexploitation, which has significant implications for domestic and agricultural water supply [9–12]. Given the critical role of groundwater in supporting human and ecological needs, the sustainable use of groundwater resources has become an urgent issue in arid and semiarid regions worldwide [2]. Thus, understanding the hydrochemical quality of groundwater and the mechanisms controlling it is essential for ensuring water supply security and promoting agricultural sustainability.

The natural hydrochemical composition of groundwater is shaped by various factors, including recharge water, aquifer lithology, and climate conditions [13]. In arid and semiarid regions, water resources are predominantly replenished by atmospheric precipitation and mountain meltwater [14]. Groundwater inherits its hydrochemical composition characteristics (e.g., pH, TDS, ion concentrations) from these recharge waters [15]. Meanwhile, limited recharge leads to slow groundwater circulation, extended aquifer residence times, and substantial water-rock interactions. The hyper-arid climate and intense evaporation accelerate groundwater evolution and increase its salinity [16]. The high salinity would limit the availability of these precious groundwater resources for various usages in arid and semiarid regions. For instance, prolonged use of high-salinity groundwater for irrigation can cause hazards like soil salinization, soil permeability destruction, and ultimately lead to reduced crop yields and compromised agricultural sustainability [17]. Additionally, global climate change is a pivotal factor influencing the hydrochemical composition of groundwater in arid and semi-arid regions that with fragile groundwater environments [18]. Glacier melt and permafrost thaw in mountainous regions complicate groundwater circulation in arid areas, impacting the chemical composition and quality of groundwater [19–21].

Beyond natural factors, groundwater hydrochemical quality faces threats from human activities [22], including agricultural practices and industrial wastewater discharge, which are especially pronounced in arid and semiarid regions [16]. Human activities can disturb the hydrochemical composition of groundwater both directly and indirectly [23,24]. Direct

contaminant inputs represent the most extensive and severe anthropogenic disturbances to groundwater environments [25]. These direct anthropogenic contaminants threating groundwater quality can be from diverse sources, such as urban sewage, agricultural practices, landfills, industry, and mining, and have been widely reported in both developing and developed countries globally [26–31]. Indirectly, human activities impact groundwater chemistry by causing hydrodynamic disturbances and aquatic environmental shifts, which trigger the release of substances from soils and aquifers, as well as alterations in hydrochemical processes [32–35]. The interplay of natural processes and human activities results in spatial variations and complexities in groundwater chemistry [36], which is particularly pronounced in arid and semiarid regions with intensive agricultural practices [37].

Arid and semiarid watersheds are characterized by low precipitation, high evaporation rates, and sparse vegetation [14]. These conditions lead to limited surface water availability, making groundwater the primary source of water for various uses [15]. However, groundwater quality in the lower reaches of arid endorheic watersheds is highly susceptible to harsh environmental conditions, frequently threatened by evaporation, extended water-rock interactions, and the consequent salinity [14,38]. Additionally, the lower reaches often serve as the primary agricultural areas in arid basins due to their advantageous soil and water conditions, resulting in anthropogenic disturbances to groundwater chemistry and threats to groundwater quality there [39,40]. Previous studies have primarily concentrated on the hydrogeochemical processes and factors influencing groundwater quality across entire watersheds in arid regions [14,15], with limited focus on the lower reaches. The Qaidam Basin, situated on the northeastern Tibetan Plateau, is a typical arid closed basin with numerous endorheic watersheds [41]. Water resources in the basin, whether above or beneath the ground surface, primarily originate from river water at the mountain pass [15]. Precipitation in the basin contributes very limited recharge to both surface water and groundwater [42], which can be considered negligible. Groundwater sustains the water needs of ecosystems and human community [43,44], leading to the formation of oases and human settlements primarily in the lower watersheds where groundwater is shallow. However, groundwater salinity and contamination are increasing in the lower watershed of Qaidam Basin [45] and similar regions worldwide [46–48]. Comprehensive understanding of groundwater chemistry and its quality suitability for various usages in these regions is essential for effective groundwater management and the rational exploitation and sustainable development of arid regions.

Hydrogeochemical analyses, including hydrochemical diagrams, statistical analysis, and hydrogeochemical modeling, are robust approaches to elucidate water chemistry status and quality [49]. Hydrochemical diagrams, such as Gibbs diagrams, end-member diagrams, and ionic ratio diagrams, graphically reveal the mechanisms controlling groundwater chemical composition [14,50–52]. Statistical analysis, particularly correlation analysis, quantifies relationships among hydrochemical indicators and further reveals the formation mechanisms of groundwater chemistry [53]. Hydrogeochemical modeling, including saturation index simulation and inverse modeling, helps to understand the complex interactions between groundwater and its surrounding geological environment [14,38]. Groundwater quality for various uses can be evaluated using multiple methods, such as Single Factor Water Quality Assessment and Water Quality Index. The Single Factor Water Quality Assessment is straightforward and useful for identifying the most polluted parameter, but it may overlook other significant factors. The Water Quality Index (WQI) provides a more comprehensive evaluation by integrating multiple parameters into a single score, offering a holistic view of groundwater quality [22]. The Entropy-Weight Water Quality Index (EWQI) further enhances this by assigning weights to parameters based on their variability, making it a robust tool for complex groundwater systems [54].

This study concentrates on the hydrochemical properties, quality, and controlling mechanisms of phreatic groundwater in the lower reaches of arid basins, where extensive agricultural lands are located. The specific aims are to: (1) clarify the physicochemical properties of groundwater in the phreatic aquifers of agricultural lower reaches in arid inland watersheds; (2) assess the suitability of groundwater quality for domestic and agricultural usages; and (3) reveal the impact of natural and anthropogenic processes on groundwater chemistry. This research could enhance the understanding of groundwater chemistry in the lower reaches of arid endorheic watersheds, offering scientific insights for managing groundwater resources in present study area and similar arid regions worldwide.

2. Description Study Area

The study area is located in the lower reaches of the Bayin Watershed, situated in the northeastern Qaidam Basin on the Tibetan Plateau (Figure 1). It covers an area of approximately 192.14 km^2. The terrain in this region is relatively flat, with a topography that slopes from higher elevations in the north to lower elevations in the south, ranging in altitude from 2853 to 2875 m. The study area has a typical plateau continental climate, characterized by significant diurnal temperature variations, aridity, and scarce precipitation [45]. The annual temperature in the region ranges from −11.1 °C to 16.2 °C, with an average of 3.8 °C. Precipitation varies between 283.7 mm and 470.5 mm, averaging 202.9 mm. The annual average evaporation rate reaches approximately 1430 mm, while the average air humidity is only about 35%. Villages are predominantly situated in the northern part of the study area, where agriculture and animal husbandry are the primary economic activities. The southern part of the study area is characterized by extensive bare land with sparse vegetation, primarily consisting of salt-tolerant plants such as *Suaeda heteroptera* and *Matrimony vine*.

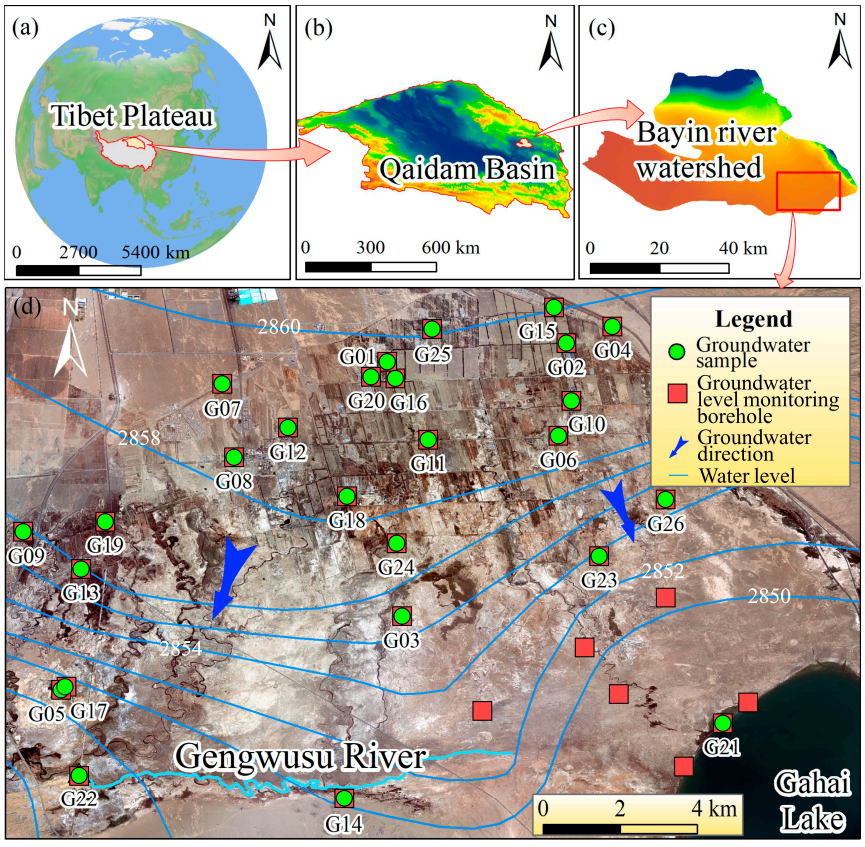


Figure 1. Map illustrating the location of (**a**) the Tibetan Plateau on Earth, (**b**) the Qaidam basin on the Tibetan Plateau, (**c**) the study area within the Qaidam basin, and (**d**) groundwater sampling sites.

The geological composition of the study area is primarily mud and clay, with sand and gravel predominantly distributed in the northern part. A small amount of groundwater flows along ancient river channels from the northwest to the southeast, ultimately draining into the Gahai Lake. Due to the fine-grained nature of the aquifer, the groundwater is shallow and flows slowly, with a hydraulic gradient of approximately 2.33‰. In some areas, groundwater overflow to the surface and converges to form the Gengwusu River in the southwest (Figure 1d). The shallow depth of groundwater and intense evaporation contribute to the unique distribution characteristics of soil salinization in the region. Groundwater in the study area is primarily replenished by precipitation and lateral recharge from upstream sources. The aquifer, influenced by its particle composition, transitions from a thick single layer to a multi-layered structure composed of sand and gravel, silt, and clay. The study area primarily relies on channel irrigation to divert high-quality river water from upstream for agricultural purposes, which is affected by groundwater salinization. However, channel irrigation is cumbersome costly in some areas. Groundwater, being the most significant water body in the region and easily accessible, offers an alternative. Therefore, clarifying the hydrochemical characteristics and regulatory mechanisms of groundwater is crucial for identifying suitable groundwater resources.

3. Materials and Methods

3.1. Sample Collection and Analysis

Twenty-six groundwater samples were collected from the unconfined aquifer between July and August 2023. The sampling locations were evenly distributed across the study area using available boreholes and wells, providing a representative reflection of the region's groundwater characteristics. To ensure the representativeness of the collected water samples, each sampling site was pumped for at least 15 min to minimize the interference of stagnant water. The in-situ physicochemical parameters (temperature, pH, electrical conductivity) of the groundwater were measured before collection. After the parameters stabilized, the target water samples were used to pre-rinse 500 mL corrosion-resistant polyethylene bottles 2–3 times, followed by sampling. The collected water samples were stored at −4 °C and transported to the laboratory for analysis within 48 h.

Water temperature, pH, and electrical conductivity (EC) were measured using a portable multi-parameter instrument (HACH HQ40d, Loveland, CO, USA). TDS and ion concentrations were analyzed in the laboratory of Groundwater Sciences and Engineering of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. Major cations were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500ce, Tokyo, Japan), while major anions (Cl^- and SO_4^{2-}) and nitrogen contaminants (NO_3^-, NO_2^- and NH_4^+)were determined by chromatography (Shimadzu LC-10ADvp, Kyoto, Japan). HCO_3^- and total dissolved solids (TDS) were measured using acid-base titration and gravimetric methods, respectively. Triplicate analyses were performed on all samples to ensure the consistency of the measured parameters. The ionic charge balance percentage error for all samples was within 10%, indicating the reliability of the test results.

3.2. Entropy-Weight Water Quality Index

The Entropy Weighted Water Quality Index (EWQI) is a method for evaluating water quality that uses information entropy theory to determine the weights of various water quality parameters [55]. The EWQI effectively reduces human interference in weight assignment, making evaluation results more objective than those derived from traditional WQI (Water Quality Index) method. The specific process can be divided into the following four steps [55].

Step 1: Build the matrix of initial eigenvalues X according to hydrochemical data.

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

where, m is the number of groundwater samples and n stands for account of hydrochemical parameters.

Step 2: Calculation of normalized matrix Y.

$$y_{ij} = \begin{cases} \frac{x_{ij} - \min(x_{ij})}{\max(x_{ij}) - \min(x_{ij})} + 0.0001 \\ \frac{\max(x_{ij}) - x_{ij}}{\max(x_{ij}) - \min(x_{ij})} + 0.0001 \end{cases} \quad (2)$$

$$Y = \begin{bmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & \cdots & y_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ y_{m1} & y_{m2} & \cdots & y_{mn} \end{bmatrix} \quad (3)$$

where, y_{ij} signify the calculated result of X at the same position.

Step 3: Quantitative calculation of information entropy and entropy weight.

$$p_{ij} = \frac{y_{ij}}{\sum_{i=1}^{m} y_{ij}} \quad (4)$$

$$e_j = -\frac{1}{\ln m} \sum_{i=1}^{m} p_{ij} \ln(p_{ij}) \quad (5)$$

$$\omega_j = \frac{1 - e_j}{\sum_{j=1}^{n} (1 - e_j)} \quad (6)$$

where, e_j and w_j represent the information entropy and entropy weight of each hydrochemical parameter, respectively.

Step 4: Calculation of *EWQI*.

$$q_{ij} = \frac{C_j}{S_j} \times 100 \quad (7)$$

$$EWQI = \sum_{j=1}^{n} \omega_j q_{ij} \quad (8)$$

where, C_j is the actual concentration of j-th hydrochemical parameter; S_j signifies the acceptable limit value.

3.3. Irrigation Water Quality Assessment

The study area is characterized by extensive farmlands, indicating significant potential for groundwater irrigation. Compared to canal irrigation, local groundwater exploitation can save time and reduce labor costs. This study employs the Irrigation Water Quality Indexes, including the Sodium Adsorption Ratio (*SAR*), Soluble Sodium Percentage (%Na) and Permeability Index (PI), to objectively evaluate the suitability of groundwater for irrigation in the study area.

The Sodium Adsorption Ratio (SAR) quantifies the extent of cation exchange reactions between irrigation water and soil. Higher *SAR* values indicates greater soil susceptibility to sodium adsorption, which can disrupt soil structure [56]. The calculation formula is as follows:

$$SAR = \frac{Na^+}{\sqrt{\frac{Mg^{2+}+Ca^{2+}}{2}}} \times 100\% \quad (9)$$

Soluble Sodium Percentage (%*Na*) can monitor the potential *Na* hazard in irrigation water. Excessive sodium (*Na*) in water can exchange with *Ca* and *Mg* in the soil, reducing soil permeability [57]. The formula for %Na is expressed below:

$$\%Na = \frac{Na^+ + K^+}{Na^+ + K^+ + Mg^{2+} + Ca^{2+}} \times 100\% \quad (10)$$

The Permeability Index (*PI*) reflects the impact of long-term use of irrigation water with high concentrations of calcium, magnesium, sodium, and bicarbonate on soil permeability [58]. The calculation formula is as follows:

$$PI = \frac{Na^+ + \sqrt{HCO_3{}^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100\% \quad (11)$$

4. Results and Discussion

4.1. Physicochemical Characteristics of Groundwater

In order to understand the physicochemical characteristics of groundwater in the study area, 13 physical and chemical parameters were statistically analysed. The variations of physical and chemical parameters are present in Table 1 and Figure 2, including the mean values, standard deviations, drinking water standard set by China [59] or the World Health Organization [60], and hydrochemical types. The pH of groundwater in the study area ranges from 7.20 to 8.43, with a mean of 7.70, indicating weakly alkaline conditions (Table 1 and Figure 2). All sampled groundwaters fall within the drinking water pH standard of 6.5–8.5 set by China [59]. The TDS values of groundwater range from 253 mg/L to 1810 mg/L, with a mean of 658 mg/L. This falls within the previously reported TDS range for phreatic groundwater in the entire watershed and is far below the maximum TDS of 8954 mg/L [61]. Most sampled groundwater in the study area is classified as fresh water, but 19.23% exceeds the permissible drinking water standard (TDS > 1000 mg/L) and is classified as brackish water (Figure 2). The EC values of groundwater in the study area range from 464 µS/cm to 2616 µS/cm, with a mean of 1054 µS/cm.

For the major cations, Na^+ is the predominant ion in groundwater, with concentrations ranging from 0.5 mg/L to 382.00 mg/L and a mean of 108.55 mg/L. Ca^{2+} was the second most abundant ion, with concentrations ranging from 28.46 mg/L to 206.41 mg/L and an average of 81.14 mg/L. The Durov diagram confirms that Ca^{2+} and Na^+ are the major cations governing the groundwater hydrochemical type (Figure 2). The concentrations of Mg^{2+} and K^+ vary from 15.19 mg/L to 78.49 mg/L and 0.00 mg/L to 10.50 mg/L, with mean values of 38.55 mg/L and 2.65 mg/L, respectively. For the major anions, $HCO_3{}^-$ is the dominant ion influencing the hydrochemical type of groundwater (Figure 2), with concentrations ranging from 6.00 mg/L to 469.85 mg/L and a mean of 262.76 mg/L (Table 1). Cl^-, as a secondary anion influencing the hydrochemical types of groundwater, varies in concentration from 6.00 mg/L to 469.85 mg/L, with a mean of 262.76 mg/L. In comparison, the concentration of $SO_4{}^{2-}$ is lower, ranging from 3.26 mg/L to 437.07 mg/L, with a mean of 118.24 mg/L. Overall, most groundwaters are characterized by fresh hydrochemistry, with hydrochemical types predominantly classified as HCO_3-Na and HCO_3-Ca types, and

only 11.54% of the sampled groundwaters exhibit Cl-Na type. This is consistent with the previously reported hydrochemical facies evolution of phreatic groundwater in the entire watershed [45].

Table 1. Summary of groundwater physicochemical indexes in the study area and corresponding drinking water standards.

Index	Min	Max	Mean	SD *	CV (%)	Guideline	% of the Samples Exceeding the Guideline
pH	7.20	8.43	7.70	0.34	4.36	6.5–8.5 **	0.00
TDS	253	1810	658	387	59	1000 **	19.23
EC	464	2616	1054	559	53	/	/
K^+	0.00	10.50	2.65	3.30	124.38	/	/
Na^+	0.50	382.00	108.55	83.10	76.55	200 **	11.54
Ca^{2+}	28.46	206.41	81.14	41.65	51.33	75 ***	42.31
Mg^{2+}	15.19	78.49	38.55	17.45	45.26	50 ***	23.08
Cl^-	3.68	701.91	162.98	163.22	100.15	250 **	19.23
SO_4^{2-}	3.26	437.07	118.24	91.52	77.40	250 **	7.69
HCO_3^-	6.00	469.85	262.76	97.36	37.05	/	/
NO_3^-	0.32	100.00	14.59	20.01	137.16	50.0 ***	3.85
NO_2^-	0.00	0.48	0.03	0.10	308.16	0.02 **	26.92
NH_4^+	0.00	0.20	0.04	0.06	156.20	0.2 **	7.69

* Standard Deviation; ** Chinese Guideline [59]; *** WHO Guideline [60].

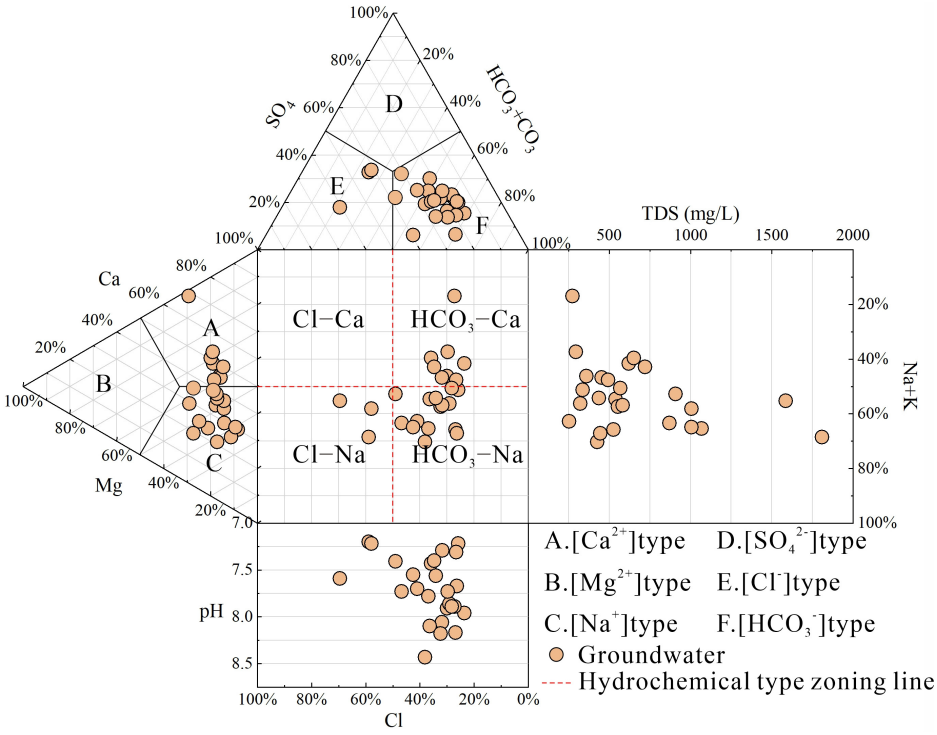


Figure 2. Durov diagram showing the physicochemical composition of groundwater in the study area.

Nitrogen is a common contaminant in groundwater in many regions worldwide [51,62,63]. Especially in agricultural areas, the extensive use of nitrogen fertilizers to boost grain production has led to nitrate contamination in agricultural groundwater through leaching [64]. The nitrate contents of groundwater in the study area have been determined in present research. The results showed that the NO_3^- content in groundwater varies between 0.32 mg/L and 100.00 mg/L, with a mean of 14.59 mg/L. Approximately 3.59% of sampled groundwaters have NO_3^- contents exceeding the drinking water quality limits of 50 mg/L set by the WHO [60]. For NO_2^-, the drinking water quality limit established by China is <0.02 mg/L [59]. The NO_2^- concentration in groundwater ranges from 0.00 mg/L to

0.48 mg/L, with an average of 0.03 mg/L, and 26.92% of the sampled groundwaters exceeded this limit in the study area. The NH_4^+ concentrations in the sampled groundwaters range from 0.00 mg/L to 0.20 mg/L, with a mean of 0.06 mg/L. Approximately 7.69% of the sampled groundwaters have NH_4^+ concentrations exceeding the permissible drinking water standard established of <0.2 mg/L set by China [59]. The above findings indicate that groundwater in the study area has been contaminated with nitrogen to some extent, highlighting the need to focus on the sources of nitrogen contamination and the processes controlling groundwater quality.

4.2. Hydrochemical Quality of Groundwater

4.2.1. Suitability of Groundwater for Domestic Usages

Groundwater is the primary source of domestic water for households in arid agricultural regions. The suitability of groundwater for domestic use is assessed using a comprehensive water quality diagram that integrates TH and TDS, along with the EWQI. The comprehensive water quality diagram [65] shows that the majority of groundwater samples in the study area are of fresh quality, comprising 80.8% of the total samples (Figure 3). A smaller proportion of groundwater is classified as brackish, representing 19.2% of the total samples. Groundwater in the study area is characterized by relatively high hardness, ranging from medium to very hard. Specifically, 46.2% of the groundwater samples are classified as moderately hard. Both hard and very hard water each account for 26.9% of the total samples. Overall, the groundwater quality in the study area is relatively good, despite its high hardness level. It is suitable for general domestic use, but excessive direct consumption is not recommended.

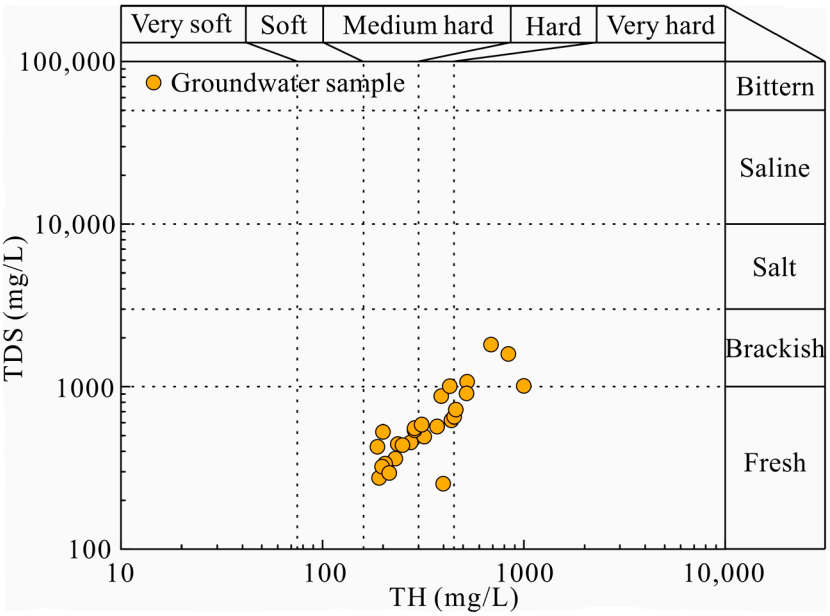


Figure 3. Relationship between TH and TDS of groundwater in the study area.

The EWQI further refines the differences in groundwater quality within the study area (Figure 4). The results indicate that the EWQI of the collected groundwater samples varies significantly, ranging from 24.82 to 211.30. Most groundwater samples have an EWQI below 100, indicating good water quality. Groundwater samples with an excellent quality grade account for 50% (i.e., 13 samples) of the total samples. Samples with a good quality grade account for 38.5% of the total samples, indicating that the groundwater in these areas is suitable for domestic use. However, 7.7% (2 samples) of the samples are of medium quality, and 3.8% (1 sample) are classified as extremely poor. Groundwater in these areas is

likely contaminated by agricultural activities and is not recommended for domestic use. The EWQI results are generally consistent with the findings from the comprehensive water quality diagram (Figure 3). Overall, most groundwater in the study area is of good quality and suitable for domestic use. However, it is advisable to avoid using groundwater from a few areas with poor quality. Boiling the water before consumption is recommended to reduce its hardness.

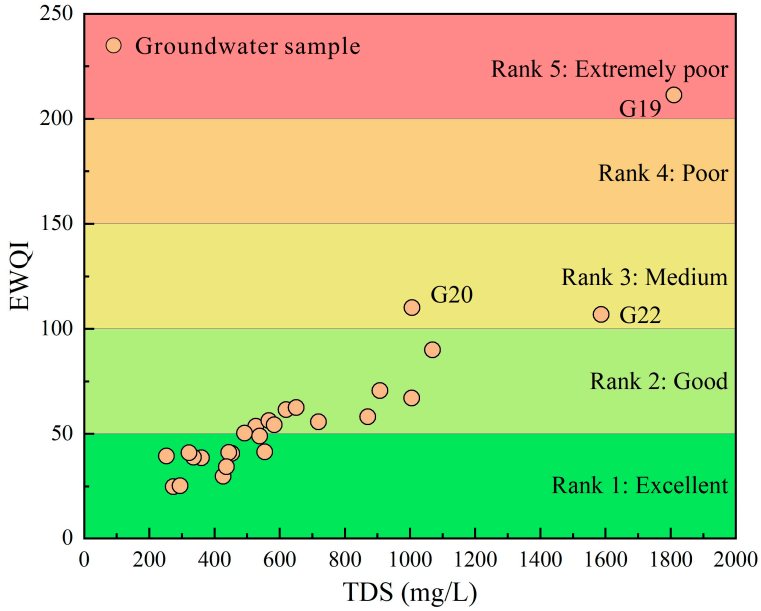


Figure 4. Relationship between TDS and EWQI of groundwater in the study area.

4.2.2. Suitability of Groundwater for Agricultural Irrigation

In arid agricultural regions, a significant proportion of water resources is allocated to irrigation. Due to the arid conditions, the supply of irrigation water heavily relies on local groundwater. The suitability of groundwater for agricultural irrigation depends on its chemical ion contents [8]. High concentrations of ions can cause irreversible soil damage. In arid areas, it is particularly important to consider the impact of evaporation on groundwater ion concentrations. The Sodium Adsorption Ratio (SAR), Percentage of Sodium (%Na), and Permeability Index (PI) are key indicators used to evaluate the suitability of groundwater for agricultural irrigation. These indices provide a comprehensive assessment from different perspectives, considering both chemical composition and potential impacts on soil structure and permeability.

SAR is utilized to assess the extent of soil degradation caused by the exchange of Na^+ with Ca^{2+} or Mg^{2+} [66]. High SAR values can lead to soil dispersion, reducing soil permeability and causing infiltration problems, which ultimately affect crop yields [1,56]. The SAR of the collected groundwater samples in the study area ranges from 0.02 to 6.32, indicating excellent groundwater quality. The USSL diagram integrates SAR with EC (Figure 5) to assess the overall sodium hazard for agricultural irrigation [67,68]. The vast majority of groundwater samples pose a low sodium risk. Among these, 38.5% (10 samples) fall into the C2S1 category, indicating a moderate salinity risk. Those in the C3S1 category account for 50.0% (13 samples) of the total groundwater samples, demonstrating a high salinity risk. A small number of groundwater samples present a moderate sodium risk, with relatively high salinity risk. Specifically, 3.8% (1 sample) of the samples fall into the C3S2 category (high salinity risk), and 7.7% (2 samples) fall into the C4S2 category (very high salinity risk). While, the overall sodium risk of groundwater in the study area is relatively low, the salinity risk is comparatively high.

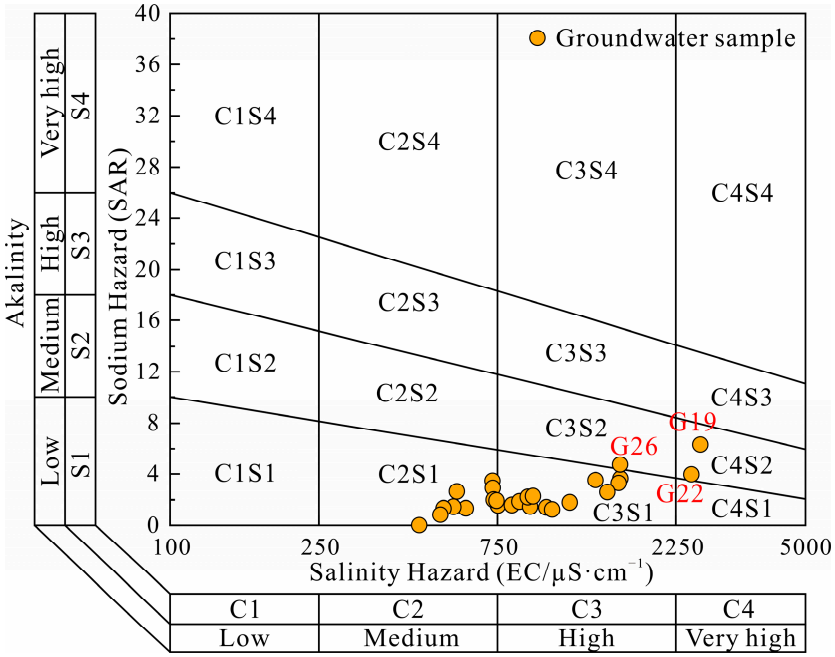


Figure 5. USSL diagram [69] classifying the irrigation quality of groundwater in the study area.

Na% is a powerful tool for evaluating the impact of Na^+ on soil permeability [1]. In the study area, the Na% of groundwater samples range from 1.22 to 54.99, falling within the acceptable range for irrigation water. The Wilcox diagram, constructing by Na% and EC [70], is introduced to evaluate the comprehensive irrigation quality of groundwater (Figure 6). It was found that 88.5% of the groundwater samples have good irrigation quality, with 38.5% classified as "Excellent Good", and 50.0% as "Good Permissible". A small proportion of groundwater samples (11.5%) may not be suitable for agricultural irrigation, with 3.8% classified as "Permissible to Doubtful" category and 7.7% as "Doubtful to Unsuitable" category. Except for these few areas, almost all groundwater in the study area is suitable for irrigation.

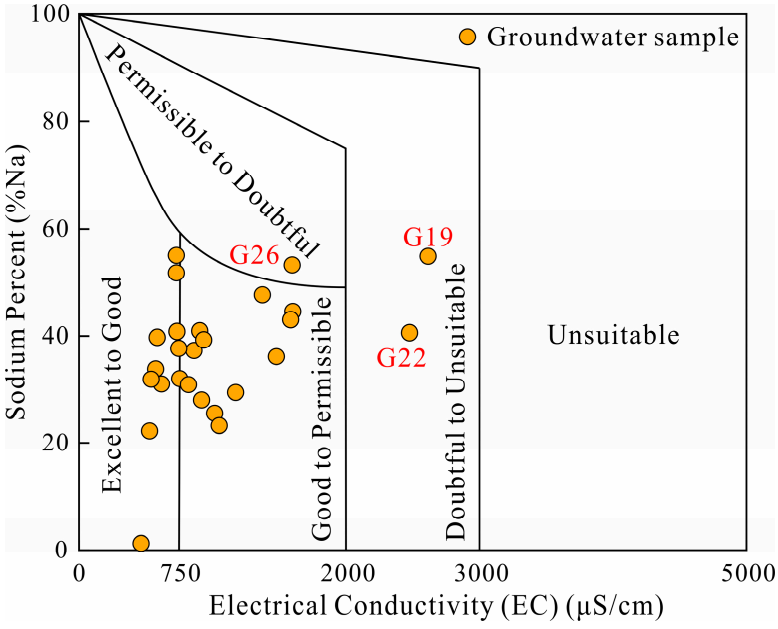


Figure 6. Wilcox diagram illustrating groundwater quality for irrigation purpose in the study area.

The Permeability Index (PI) serves as a critical metric for assessing the infiltration efficiency of irrigation water within the soil matrix [1]. In the study area, the PI values of the groundwater samples span from 41.49 to 78.20, indicating that these groundwaters are well-suited for agricultural irrigation purposes in terms of permeability. Utilizing the Doneen diagram [69], which correlates the total concentration of chemical ion with the PI, groundwater is classified into three distinct categories based on their permeability characteristics (Figure 7). The groundwater samples from the study area are distributed within Class-I and Class-II dominances. Specifically, Class-I groundwater, which exhibits superior permeability and is highly conducive to agricultural irrigation, constitutes 55.70% of the total sample population. Class-II groundwater, while still suitable for agricultural irrigation, is of slightly lower quality compared to Class-I and comprises 42.30% of the samples. The groundwater in the study area exhibits excellent permeability feature to the soil, meeting the established criteria for agricultural irrigation water quality.

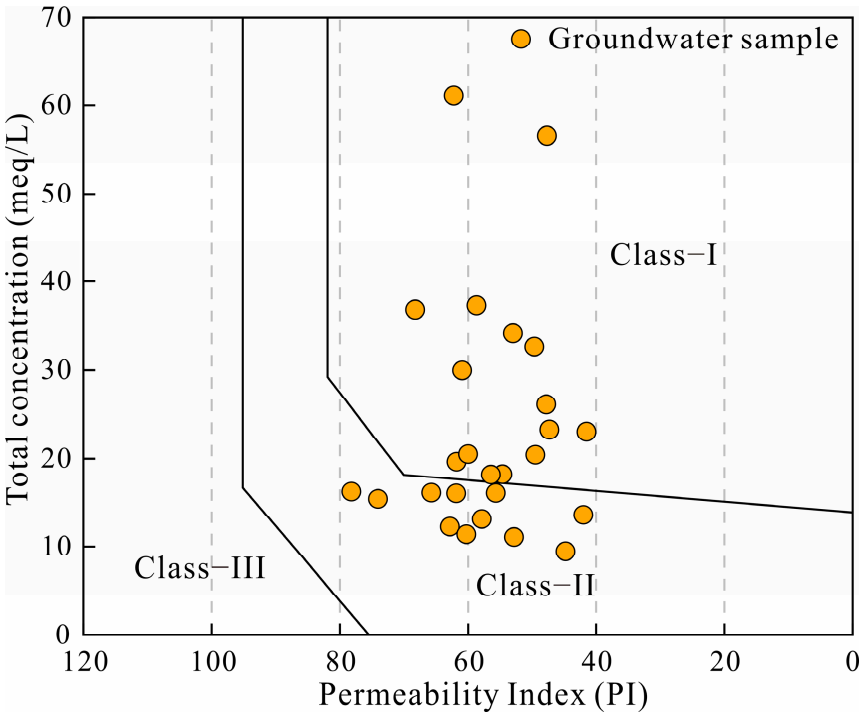


Figure 7. Doneen diagram illustrating groundwater quality for irrigation purpose in the study area.

Overall, 88.5% of the groundwater in the study area has good water quality and soil permeability characteristics, making it suitable for agricultural irrigation. These waters have a low sodium hazard, which essentially does not impair soil permeability. However, there is a certain salinity threat associated with long-term irrigation. A small proportion (11.5%) of the groundwater's suitability for agricultural irrigation is debatable, as these waters present a higher salinity threat and carry a certain sodium risk.

4.3. Mechanisms Controlling Groundwater Chemistry

Clarifying the formation mechanisms of groundwater hydrochemistry can enable targeted implementation of water resource management measures. The Gibbs diagrams, which are constructed by $Na^+/(Na^+{+}Ca^{2+})$ versus TDS and $Cl^-/(Cl^-{+}HCO_3^-)$ versus TDS, were introduced to reveal the major natural mechanisms controlling groundwater chemistry [49]. It can be seen that nearly all sampled groundwaters are situated in the area from the rock dominance to the evaporation dominance (Figure 8). This indicates that under natural conditions, rock-water interactions and evaporation are the primary

factors governing the hydrochemical composition of groundwater in the study area. The characteristics of groundwater in the study area further confirm the reliability of this conclusion. The slow velocity of groundwater flow in the study area allows sufficient time for material exchange between groundwater and surrounding aquifers mediums. Additionally, the shallow depth of groundwater, combined with slow flow velocity, makes it highly susceptible to evaporation. The influence of precipitation on the hydrochemical composition of groundwater in the study area is minimal, due to its location in the arid region with extremely scarce precipitation.

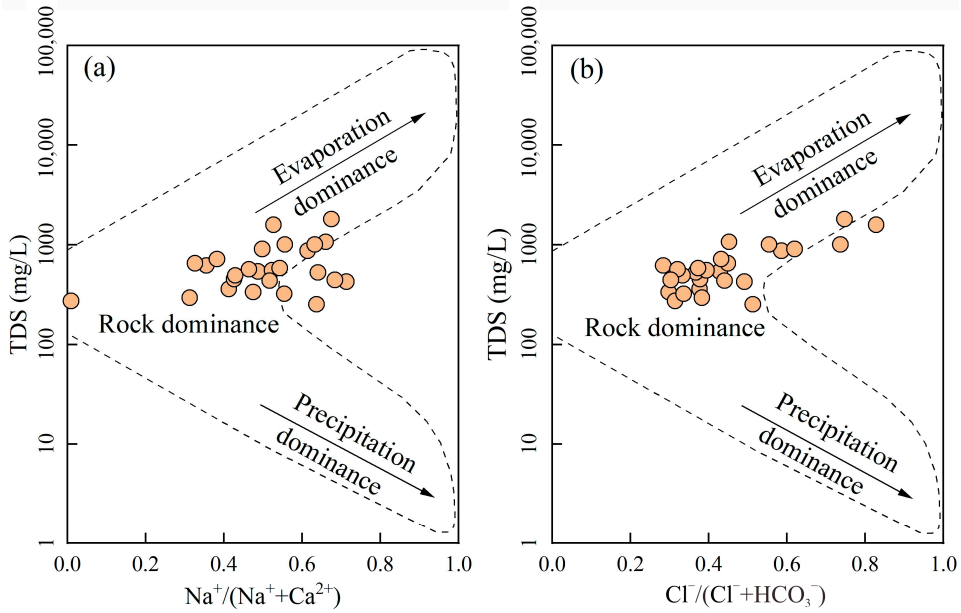


Figure 8. Gibbs plots of (**a**) $Na^+/(Na^+ + Ca^{2+})$ versus TDS, and (**b**) $Cl^-/(Cl^- + HCO_3^-)$ versus TDS of groundwater in the study area.

In addition to natural sources, anthropogenic activities such as domestic sewage discharge and fertilizer application also impact the hydrochemical composition of groundwater [26,27]. Nitrate is a primary hydrochemical indicator for assessing whether groundwater has been affected by human activities. Typically, the concentration of nitrate in the natural environment is below 10 mg/L [50]. Concentrations exceeding this threshold are considered indicative of anthropogenic pollution. As shown in Figure 9, approximately 34.6% of groundwater samples have nitrate concentrations exceeding 10 mg/L, indicating that human activities have influenced the hydrochemical composition of groundwater [71]. Furthermore, a slight positive correlation between groundwater nitrate content and TDS further suggests that human activities (such as agricultural fertilizers and municipal sewage) have increased the ion content in the study area's groundwater. Groundwater samples G5, G8, G9, G10, G12, G16, G18, G19, and G20, which have high nitrogen content, are located in the northern and western parts of the study area, characterized by extensive agricultural activities. Compared to the southern region, these areas have faster groundwater flow velocities and greater groundwater depth, leading to reduced water-rock interaction and evaporation. Consequently, agricultural activities are identified as the primary cause for the elevated TDS in these groundwaters. Groundwater samples G22 and G26 are located in the south and east of the study area, respectively, which are bare land concentration areas. The lower nitrate content indicates that the high TDS in these groundwaters is dominated by water-rock interactions and evaporation.

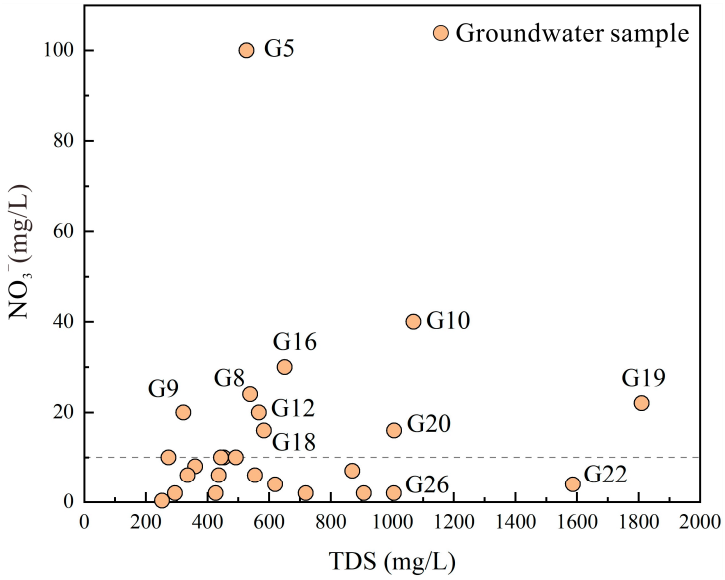


Figure 9. Relationship between TDS and NO_3^- of groundwater in the study area.

As shown in Figure 10, most groundwater samples fall within the transition zone between agricultural activities and evaporation, indicating that both evaporation and agricultural activities jointly influence the hydrochemical composition of groundwater [72]. Only one groundwater sample (G07) is entirely within the agricultural activity zone. This may be because the sample location is in the upstream area of the study area, where the groundwater depth exceeds the critical depth for evaporation, thereby diminishing the impact of evaporation on the hydrochemical composition of groundwater. Groundwater samples G09 and G16 are both located near the farm areas of the study region, while G22 and G26 are situated in the bare land areas. It can be observed that as the groundwater sampling sites move progressively southward, the groundwater samples in the figure gradually shift from being influenced by agricultural activities to being dominated by evaporation process. Groundwater sample G11 is located adjacent to the municipal sewage dominance of the diagram (Figure 10), indicating that it is likely affected by the village's municipal sewage.

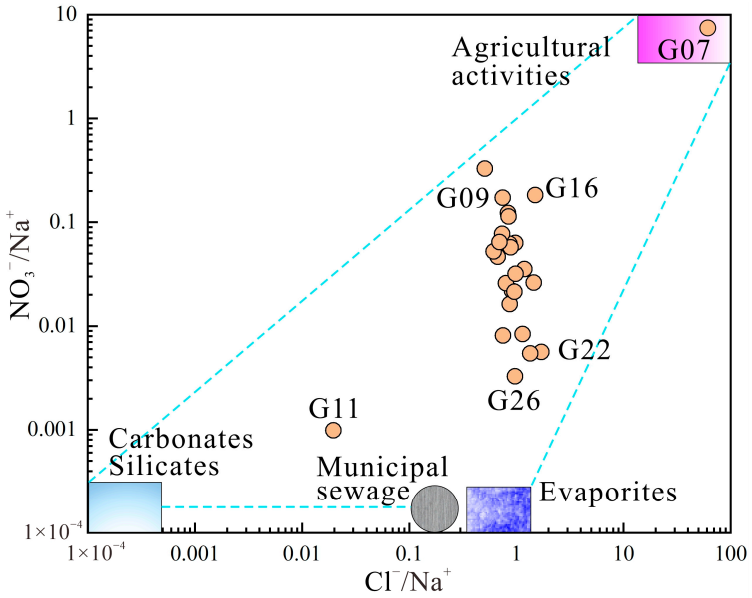
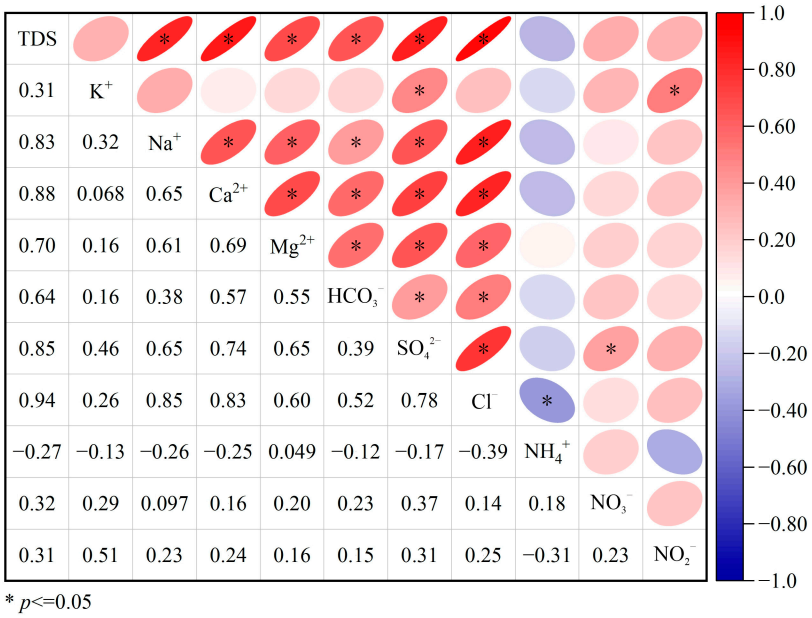


Figure 10. Relationship between Cl^-/Na^+ and NO_3^-/Na^+ of groundwater in the study area.

As shown in Figure 11, there is a significant positive correlation between major cations and major anions, indicating a consistent source, such as water-rock interaction and evaporation. However, the correlation between K^+ and the other major ions is not particularly significant. Moreover, the correlation coefficient between K^+ and nitrate is 0.29, which is relatively high compared to the correlations between nitrate and the other major ions. This suggests that the use of potassium fertilizers may be another source of K^+ for groundwater in the study area. The positive correlation between nitrate and major ions suggests that agricultural activities, while increasing the nitrate content in groundwater, also introduce other major ions. NH_4^+ exhibits a slight negative correlation with other ions, indicating that it may have a different origin from them. Sheep are a common livestock in the local area, predominantly raised in a free-range manner. The indiscriminate excretion of sheep manure may be a primary source of NH_4^+ in groundwater.



* p<=0.05

Figure 11. Correlation coefficient for hydrochemical parameters of groundwater in the study area.

4.4. Implication for Groundwater Sustainable Development Management in Arid Lower Reaches

This research takes a typical arid endorheic watershed on Tibetan Plateau as an example to investigate the hydrochemical status, quality availability for various purposes and formation mechanisms of the lower reaches of arid watersheds that with dense agricultural practices. Information obtained in this research is crucial for groundwater resource development and management in present study arid lower reaches and similar regions worldwide. Gaining insights into the groundwater chemistry of the study area clarifies the interplay between natural and human factors affecting it, guiding policy implementation in arid and semiarid regions as follows:

(1) Controlling groundwater salinization. This research reveals that phreatic groundwater resource in the lower reaches of arid endorheic watersheds confronts significant salination threats from both natural evaporation and agricultural irrigation. Preventing salinization is key to the scientific management and sustainable use of groundwater resources in arid inland areas [52]. Therefore, managing groundwater levels and adopting rational agricultural practices are recommended for controlling groundwater salinization in arid basins.

(2) Reducing nitrogen contamination. As discussed, groundwater quality is compromised by various human-derived nitrogen contaminants, such as NO_3^-, NO_2^-, and NH_4^+. These contaminants, predominantly from agricultural fertilizers, are common in farming

practices worldwide [63,73,74], not just in arid regions. However, the arid and endorheic nature of these basins facilitates the accumulation of nitrogen contaminants in aquifers, as groundwater circulation is limited, making their removal difficult [75]. Consequently, nitrogen contaminants accumulated in prolonged agricultural practices would pose a significant health risk to communities reliant on groundwater for their daily domestic water supply. Actions should be taken to mitigate nitrogen contamination. For example, adopting precision agriculture techniques—such as optimized fertilizer application rates and timing—can minimize excess nutrient leaching. Implementing crop rotation and intercropping with nitrogen-fixing plants enhances soil nitrogen retention. Strengthening groundwater monitoring networks and enforcing region-specific fertilizer regulations are critical to safeguarding water quality in vulnerable arid basins. Public awareness campaigns on sustainable farming practices and safe groundwater use should also be prioritized to ensure long-term community health.

(3) Allocating groundwater resource rationally. Despite salinity and nitrogen contamination challenges in the lower agricultural areas of arid watersheds, groundwater can sustain agricultural and community development in these water-scarce regions with prudent groundwater resource management [76]. Groundwater resources should be allocated based on their suitability for different uses. Rational use and allocation of various quality groundwater resources, instead of indiscriminate exploitation of high-quality groundwater, are crucial for securing water supply and fostering sustainable management in arid regions.

5. Conclusions

This research takes a typical arid endorheic watershed on Tibetan Plateau to get insights into the hydrochemcial features, quality and formation mechanisms of phreatic groundwater in the lower reach of arid inland basins. The research finds that phreatic groundwater in the lower reach of Bayin watershed is slightly alkaline (pH 7.20–8.43), predominantly fresh (TDS $\leq$ 1000 mg/L; 80.8% samples), and classified as HCO_3-Ca and HCO_3-Na types. Elevated nitrogen contamination is observed with 3.59%, 26.92%, and 7.69% of samples exceeding permissible limits for NO_3^- (50 mg/L), NO_2^- (0.02 mg/L), and NH_4^+ (0.2 mg/L), respectively. Water quality varies widely (EWQI: 24.82–211.30), with 88.5% of samples suitable for drinking (excellent or good quality). Salinity poses the primary irrigation risk (38.5% moderate, 53.8% high, 7.7% very high risk), while sodium and permeability hazards are negligible. Hydrochemical composition is governed by natural rock-water interactions and evaporation, with human activities (agricultural practices) elevating TDS in northern irrigated zones and nitrogen levels watershed-wide. Management priorities include mitigating agricultural salinity, nitrogen pollution, and evaporation-driven salinization in southeastern areas. These insights are critical for sustainable groundwater use in the lower reaches of arid inland basins.

Author Contributions: Z.Z.: Conceptualization, Methodology, Formal analysis, Writing–original draft; G.L.: Field investigation, Methodology, Formal analysis; G.Q.: Field investigation, Formal analysis, Data Curation, Methodology; H.C. (Huijuan Chen): Field investigation, Formal analysis, Methodology; H.C. (Huizhu Chen): Methodology, Writing—Reviewing and Editing; W.H.: Field investigation, Formal analysis; S.Y.: Field investigation, Formal analysis; J.W.: Field investigation, Data Curation, Methodology, Formal analysis; Y.Z.: Field investigation, Methodology, Formal analysis; D.Z.: Methodology, Writing—Reviewing and Editing; Y.L.: Formal analysis, Methodology; Y.X.: Conceptualization, Writing—Reviewing and Editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Key Lab of Geo-environment of Qinghai Province (Grant No. 2023-KJ-15; 2024-KJ-06); the Provincial-Ministerial Cooperative Project of the Ministry of Natural Resources of the People's Republic of China (2024ZRBSHZ020); the Kunlun Talents—Science and

Technology Leading Talents Program of Qinghai Province (Grant to Zhen Zhao); the National Natural Science Foundation of China (42477059); the MOE Key Laboratory of Groundwater Circulation and Environmental Evolution, China University of Geosciences (Beijing) (2023-004); the Innovative Practice Bases of Geological Engineering and Surveying Engineering of Southwest Jiaotong University (YJG-2022-JD04).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of the present study will be provided upon request by the corresponding author.

Acknowledgments: The authors would like to thank the editors and anonymous reviewers for their critical comments and suggestions which greatly helped us to improve the present manuscript.

Conflicts of Interest: Authors Zhen Zhao, Guangxiong Qin, Huijuan Chen, Shaokang Yang and Dongyang Zhao were employed by the company Qinghai 906 Engineering Survey and Design Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Tang, L.; Yao, R.; Zhang, Y.; Ding, W.; Wang, J.; Kang, J.; Liu, G.; Zhang, W.; Li, X. Hydrochemical analysis and groundwater suitability for drinking and irrigation in an arid agricultural area of the Northwest China. *J. Contam. Hydrol.* **2023**, *259*, 104256. [CrossRef] [PubMed]
2. Qi, S.; Feng, Q.; Shu, H.; Liu, W.; Zhu, M.; Zhang, C.; Yang, L.; Yin, Z. Redistribution effect of irrigation on shallow groundwater recharge source contributions in an arid agricultural region. *Sci. Total Environ.* **2023**, *865*, 161106. [CrossRef] [PubMed]
3. Heiß, L.; Bouchaou, L.; Tadoumant, S.; Reichert, B. Index-based groundwater vulnerability and water quality assessment in the arid region of Tata city (Morocco). *Groundw. Sustain. Dev.* **2020**, *10*, 100344. [CrossRef]
4. Ershadfath, F.; Shahnazari, A.; Sarjaz, M.R.; Andaryani, S.; Trolle, D.; Olesen, J.E. Blue and green water availability under climate change in arid and semi-arid regions. *Ecol. Inform.* **2024**, *82*, 102743. [CrossRef]
5. Pandey, S.; Mohapatra, G.; Arora, R. Groundwater quality, human health risks and major driving factors in arid and semi-arid regions of Rajasthan, India. *J. Clean. Prod.* **2023**, *427*, 139149. [CrossRef]
6. Han, J.; Zhang, H.; Zhang, B. Volnerability assessment of shallow groundwater of Nalenggele alluvial fan, Qaidam Basin. *J. Salt Lake Res.* **2023**, *31*, 10–17. [CrossRef]
7. Eslami, F.; Yaghmaeian, K.; Mohammadi, A.; Salari, M.; Faraji, M. An integrated evaluation of groundwater quality using drinking water quality indices and hydrochemical characteristics: A case study in Jiroft, Iran. *Environ. Earth Sci.* **2019**, *78*, 314. [CrossRef]
8. Satheeskumar, V.; Subramani, T.; Lakshumanan, C.; Roy, P.D.; Karunanidhi, D. Groundwater chemistry and demarcation of seawater intrusion zones in the Thamirabarani delta of south India based on geochemical signatures. *Environ. Geochem. Health* **2021**, *43*, 757–770. [CrossRef]
9. Barbieri, M.; Barberio, M.D.; Banzato, F.; Billi, A.; Boschetti, T.; Franchini, S.; Gori, F.; Petitta, M. Climate change and its effect on groundwater quality. *Environ. Geochem. Health* **2023**, *45*, 1133–1144. [CrossRef]
10. Ahmed, M.; Chen, Y.; Khalil, M.M. Isotopic composition of groundwater resources in arid environments. *J. Hydrol.* **2022**, *609*, 127773. [CrossRef]
11. Chakma, S.; Hossain, M.N.; Islam, M.K.; Hossain, M.M.; Sarker, M.N.I. Water Scarcity, Seasonal Variation and Social Conflict in Mountain Regions of Bangladesh. *Grassroots J. Nat. Resour.* **2021**, *4*, 62–79. [CrossRef]
12. El-Anwar, E.A.A.; Salman, S.A. Hydrochemical modeling of groundwater quality from Sinai, eastern and western deserts, Egypt. *Model. Earth Syst. Environ.* **2022**, *8*, 4427–4439. [CrossRef]
13. Tao, L.; Zhang, Y.; Yuan, X.; Chen, Q.; Yu, J.; Ma, Y.; Liu, H.; Tu, C. Hydrological processes in multi-layered aquifers of a karst watershed with coal mining activity: Insights from hydrochemistry and isotopes. *J. Hydrol. Reg. Stud.* **2024**, *56*, 102016. [CrossRef]
14. Xiao, Y.; Shao, J.; Frape, S.K.; Cui, Y.; Dang, X.; Wang, S.; Ji, Y. Groundwater origin, flow regime and geochemical evolution in arid endorheic watersheds: A case study from the Qaidam Basin, northwestern China. *Hydrol. Earth Syst. Sci.* **2018**, *22*, 4381–4400. [CrossRef]
15. Xiao, Y.; Zhang, Y.; Yang, H.; Wang, L.; Han, J.; Hao, Q.; Wang, J.; Zhao, Z.; Hu, W.; Wang, S.; et al. Interaction regimes of surface water and groundwater in a hyper-arid endorheic watershed on Tibetan Plateau: Insights from multi-proxy data. *J. Hydrol.* **2024**, *644*, 132020. [CrossRef]

16. Jia, Y.; Xi, B.; Jiang, Y.; Guo, H.; Yang, Y.; Lian, X.; Han, S. Distribution, formation and human-induced evolution of geogenic contaminated groundwater in China: A review. *Sci. Total Environ.* **2018**, *643*, 967–993. [CrossRef]
17. Majeed, A.; Muhammad, Z. Salinity: A Major Agricultural Problem—Causes, Impacts on Crop Productivity and Management Strategies. In *Plant Abiotic Stress Tolerance: Agronomic, Molecular and Biotechnological Approaches*; Hasanuzzaman, M., Hakeem, K.R., Nahar, K., Alharby, H.F., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 83–99. [CrossRef]
18. Fallahi, M.M.; Shabanlou, S.; Rajabi, A.; Yosefvand, F.; IzadBakhsh, M.A. Effects of climate change on groundwater level variations affected by uncertainty (case study: Razan aquifer). *Appl. Water Sci.* **2023**, *13*, 143. [CrossRef]
19. Dao, P.U.; Heuzard, A.G.; Le, T.X.H.; Zhao, J.; Yin, R.; Shang, C.; Fan, C. The impacts of climate change on groundwater quality: A review. *Sci. Total Environ.* **2024**, *912*, 169241. [CrossRef]
20. Yi, B.; Liu, J.; He, W.; Lü, X.; Cao, X.; Chen, X.; Zeng, X.; Zhang, Y. Optical variations of dissolved organic matter due to surface water—Groundwater interaction in alpine and arid Datonghe watershed. *Sci. Total Environ.* **2023**, *864*, 161036. [CrossRef]
21. Kumar, R.; Manzoor, S.; Vishwakarma, D.K.; Al-Ansari, N.; Kushwaha, N.L.; Elbeltagi, A.; Sushanth, K.; Prasad, V.; Kuriqi, A. Assessment of Climate Change Impact on Snowmelt Runoff in Himalayan Region. *Sustainability* **2022**, *14*, 1150. [CrossRef]
22. Salam, M.; Bo, D.; Alam, F.; Uddin, I.; Hossain, M.N.; Hayat, F.; Ullah, W. Examining drinking water quality: Analysis of physico-chemical properties and bacterial contamination with health implications for Shangla district, Khyber Pakhtunkhwa, Pakistan. *Environ. Geochem. Health* **2024**, *46*, 209. [CrossRef] [PubMed]
23. Peng, C.; He, J.-T.; Wang, M.-L.; Zhang, Z.-G.; Wang, L. Identifying and assessing human activity impacts on groundwater quality through hydrogeochemical anomalies and NO_3^-, NH_4^+, and COD contamination: A case study of the Liujiang River Basin, Hebei Province, P.R. China. *Environ. Sci. Pollut. Res.* **2018**, *25*, 3539–3556. [CrossRef] [PubMed]
24. Akhtar, N.; Syakir Ishak, M.I.; Bhawani, S.A.; Umar, K. Various Natural and Anthropogenic Factors Responsible for Water Quality Degradation: A Review. *Water* **2021**, *13*, 2660. [CrossRef]
25. Kurwadkar, S.; Kanel, S.R.; Nakarmi, A. Groundwater pollution: Occurrence, detection, and remediation of organic and inorganic pollutants. *Water Environ. Res.* **2020**, *92*, 1659–1668. [CrossRef]
26. Mao, H.; Wang, G.; Liao, F.; Shi, Z.; Huang, X.; Li, B.; Yan, X. Geochemical evolution of groundwater under the influence of human activities: A case study in the southwest of Poyang Lake Basin. *Appl. Geochem.* **2022**, *140*, 105299. [CrossRef]
27. Nath, A.; Samanta, S.; Banerjee, S.; Danda, A.A.; Hazra, S. Threat of arsenic contamination, salinity and water pollution in agricultural practices of Sundarban Delta, India, and mitigation strategies. *SN Appl. Sci.* **2021**, *3*, 560. [CrossRef]
28. Brand, J.H.; Spencer, K.L. Potential pollution risks of historic landfills in England: Further analysis of climate change impacts. *WIREs Water* **2024**, *11*, e1706. [CrossRef]
29. Ullah, Z.; Rashid, A.; Ghani, J.; Nawab, J.; Zeng, X.-C.; Shah, M.; Alrefaei, A.F.; Kamel, M.; Aleya, L.; Abdel-Daim, M.M.; et al. Groundwater contamination through potentially harmful metals and its implications in groundwater management. *Front. Environ. Sci.* **2022**, *10*, 1021596. [CrossRef]
30. Cao, S.; Fei, Y.; Tian, X.; Cui, X.; Zhang, X.; Yuan, R.; Li, Y. Using isotopes of nitrogen and oxygen to trace groundwater nitrate contamination and contribution analysis: Exemplified by the Nanyang District. *Hydrogeol. Eng. Geol.* **2019**, *46*, 82–91. [CrossRef]
31. Salam, M.; Alam, F.; Hossain, M.N.; Saeed, M.A.; Khan, T.; Zarin, K.; Rwan, B.; Ullah, W.; Khan, W.; Khan, O. Assessing the drinking water quality of educational institutions at selected locations of district Swat, Pakistan. *Environ. Earth Sci.* **2021**, *80*, 322. [CrossRef]
32. AghaKouchak, A.; Mirchi, A.; Madani, K.; Di Baldassarre, G.; Nazemi, A.; Alborzi, A.; Anjileli, H.; Azarderakhsh, M.; Chiang, F.; Hassanzadeh, E.; et al. Anthropogenic Drought: Definition, Challenges, and Opportunities. *Rev. Geophys.* **2021**, *59*, e2019RG000683. [CrossRef]
33. Li, J.; Wang, Y.; Zhu, C.; Xue, X.; Qian, K.; Xie, X.; Wang, Y. Hydrogeochemical processes controlling the mobilization and enrichment of fluoride in groundwater of the North China Plain. *Sci. Total Environ.* **2020**, *730*, 138877. [CrossRef] [PubMed]
34. Guo, H.; Li, W.; Wang, L.; Chen, Y.; Zang, X.; Wang, Y.; Zhu, J.; Bian, Y. Present situation and research prospects of the land subsidence driven by groundwater levels in the North China Plain. *Hydrogeol. Eng. Geol.* **2021**, *48*, 162–171. [CrossRef]
35. Taucare, M.; Viguier, B.; Figueroa, R.; Daniele, L. The alarming state of Central Chile's groundwater resources: A paradigmatic case of a lasting overexploitation. *Sci. Total Environ.* **2024**, *906*, 167723. [CrossRef] [PubMed]
36. Mao, H.; Wang, G.; Rao, Z.; Liao, F.; Shi, Z.; Huang, X.; Chen, X.; Yang, Y. Deciphering spatial pattern of groundwater chemistry and nitrogen pollution in Poyang Lake Basin (eastern China) using self-organizing map and multivariate statistics. *J. Clean. Prod.* **2021**, *329*, 129697. [CrossRef]
37. Mohammed, A.M.; Refaee, A.; El-Din, G.K.; Harb, S. Hydrochemical characteristics and quality assessment of shallow groundwater under intensive agriculture practices in arid region, Qena, Egypt. *Appl. Water Sci.* **2022**, *12*, 92. [CrossRef]
38. Yang, N.; Wang, G.; Shi, Z.; Zhao, D.; Jiang, W.; Guo, L.; Liao, F.; Zhou, P. Application of Multiple Approaches to Investigate the Hydrochemistry Evolution of Groundwater in an Arid Region: Nomhon, Northwestern China. *Water* **2018**, *10*, 1667. [CrossRef]
39. Adimalla, N. Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. *Hum. Ecol. Risk Assess.* **2020**, *26*, 310–334. [CrossRef]

40. Frommen, T.; Groeschke, M.; Nölscher, M.; Koeniger, P.; Schneider, M. Anthropogenic and geogenic influences on peri-urban aquifers in semi-arid regions: Insights from a case study in northeast Jaipur, Rajasthan, India. *Hydrogeol. J.* **2021**, *29*, 1261–1278. [CrossRef]
41. Yang, N.; Wang, G. Spatial variation of water stable isotopes of multiple rivers in southeastern Qaidam Basin, northeast Qinghai-Tibetan Plateau: Insights into hydrologic cycle. *J. Hydrol.* **2024**, *628*, 130464. [CrossRef]
42. Zhao, D.; Wang, G.; Liao, F.; Yang, N.; Jiang, W.; Guo, L.; Liu, C.; Shi, Z. Groundwater-surface water interactions derived by hydrochemical and isotopic (222Rn, deuterium, oxygen-18) tracers in the Nomhon area, Qaidam Basin, NW China. *J. Hydrol.* **2018**, *565*, 650–661. [CrossRef]
43. Yang, N.; Wang, G.; Hou, E.; Guo, L.; Xiong, L.; Song, X. Triple isotopes (δD, $\delta^{18}O$, $\delta^{17}O$) characteristic of river water and groundwater in an arid watershed from Qaidam Basin, Northwestern China: Implications for hydrological cycle. *Sci. Total Environ.* **2024**, *927*, 172229. [CrossRef] [PubMed]
44. Tan, H.; Rao, W.; Chen, J.; Su, Z.; Sun, X.; Liu, X. Chemical and isotopic approach to groundwater cycle in western Qaidam Basin, China. *Chin. Geogr. Sci.* **2009**, *19*, 357–364. [CrossRef]
45. Zhao, W.; Lin, Y.; Zhou, P.; Wang, G.; Dang, X.; Gu, X. Characteristics of groundwater in Northeast Qinghai-Tibet Plateau and its response to climate change and human activities: A case study of Delingha, Qaidam Basin. *China Geol.* **2021**, *4*, 377–388. [CrossRef]
46. Zheng, N.; Guo, M.; Yue, W.; Teng, Y.; Zhai, Y.; Yang, J.; Zuo, R. Evaluating the impact of flood irrigation on spatial variabilities of soil salinity and groundwater quality in an arid irrigated region. *Hydrol. Res.* **2020**, *52*, 229–240. [CrossRef]
47. Rzigui, H.; Bogacki, W.; Hörmann, G.; Hachicha, M. Shallow groundwater salinization risks under climate change: FEFLOW model application in Cebala Borj-Touil irrigation zone, northern Tunisia. *J. Water Clim. Change* **2024**. [CrossRef]
48. Sanad, H.; Oueld Lhaj, M.; Zouahri, A.; Saafadi, L.; Dakak, H.; Mouhir, L. Groundwater pollution by nitrate and salinization in Morocco: A comprehensive review. *J. Water Health* **2024**, *22*, 1756–1773. [CrossRef]
49. Yu, Y.; Yan, B.; Tuo, Y.; Zhan, X.; Xie, X. Chemical evolution characteristics and influencing factors of groundwater in the saline and fresh water funnel area in Hengshui City, North China. *Sci. Rep.* **2025**, *15*, 3276. [CrossRef]
50. Ning, H.; Jiang, W.; Sheng, Y.; Wang, K.; Chen, S.; Zhang, Z.; Liu, F. Comprehensive evaluation of nitrogen contamination in water ecosystems of the Miyun reservoir watershed, northern China: Distribution, source apportionment and risk assessment. *Environ. Geochem. Health* **2024**, *46*, 278. [CrossRef]
51. Postigo, C.; Ginebreda, A.; Barbieri, M.V.; Barceló, D.; Martín-Alonso, J.; de la Cal, A.; Boleda, M.R.; Otero, N.; Carrey, R.; Solà, V.; et al. Investigative monitoring of pesticide and nitrogen pollution sources in a complex multi-stressed catchment: The lower Llobregat River basin case study (Barcelona, Spain). *Sci. Total Environ.* **2021**, *755*, 142377. [CrossRef]
52. Salman, S.A.; El-Anwar, E.A.A.; Aita, S.K.; Elnazer, A.A. Geo-environmental factors controlling groundwater hydrogeochemistry, salinization and quality in El Qaa plain coastal aquifer, Southwest Sinai, Egypt. *Environ. Dev. Sustain.* **2024**, *26*, 28591–28609. [CrossRef]
53. Shuaibu, A.; Kalin, R.M.; Phoenix, V.; Lawal, I.M. Geochemical evolution and mechanisms controlling groundwater chemistry in the transboundary Komadugu–Yobe Basin, Lake Chad region: An integrated approach of chemometric analysis and geochemical modeling. *J. Hydrol. Reg. Stud.* **2025**, *57*, 102098. [CrossRef]
54. Zheng, Y.; Wei, D.; Gan, J.; Zou, L.; Zhu, R.; Zhang, Y. Hydrochemical insights, water quality, and human health risk assessment of groundwater in a coastal area of southeastern China. *Environ. Monit. Assess.* **2024**, *196*, 959. [CrossRef] [PubMed]
55. Yang, Y.; Li, P.; Elumalai, V.; Ning, J.; Xu, F.; Mu, D. Groundwater Quality Assessment Using EWQI With Updated Water Quality Classification Criteria: A Case Study in and Around Zhouzhi County, Guanzhong Basin (China). *Expo. Health* **2022**, *15*, 825–840. [CrossRef]
56. Richards, L.A. Diagnosis and Improvement of Saline and Alkali Soils. *Soil Sci.* **1954**, *78*, 154. [CrossRef]
57. Rao, G.T.; Rao, V.V.S.G.; Sarma, V.S.; Dhakate, R.; Surinaidu, L.; Mahesh, J.; Ramesh, G. Hydrogeochemical parameters for assessment of groundwater quality in a river sub-basin. *Int. J. Environ. Sci. Technol.* **2012**, *9*, 297–310. [CrossRef]
58. Doneen, L.D. *Water Quality for Agriculture*; Department of Irrigation, University of California: Davis, CA, USA, 1964.
59. *GB/T 14848-2017*; Standards for Groundwater Quality. General Administration of Quality Supervision (GAQS): Beijing, China, 2017.
60. WHO. *Guidelines for Drinking-Water Quality, 4th Edition Incorporating the First Addendum*; World Health Organization: Geneva, Switzerland, 2017.
61. Zhang, B.; Zhao, D.; Zhou, P.; Qu, S.; Liao, F.; Wang, G. Hydrochemical Characteristics of Groundwater and Dominant Water–Rock Interactions in the Delingha Area, Qaidam Basin, Northwest China. *Water* **2020**, *12*, 836. [CrossRef]
62. Cui, R.; Zhang, D.; Hu, W.; Zhao, X.; Yan, H.; Liu, G.; Chen, A. Nitrogen in soil, manure and sewage has become a major challenge in controlling nitrate pollution in groundwater around plateau lakes, Southwest China. *J. Hydrol.* **2023**, *620*, 129541. [CrossRef]
63. Bijay, S.; Craswell, E. Fertilizers and nitrate pollution of surface and ground water: An increasingly pervasive global problem. *SN Appl. Sci.* **2021**, *3*, 518. [CrossRef]

64. Min, L.; Liu, M.; Wu, L.; Shen, Y. Groundwater Storage Recovery Raises the Risk of Nitrate Pollution. *Environ. Sci. Technol.* **2022**, *56*, 8–9. [CrossRef]
65. Yan, Y.; Zhang, Y.; Yang, S.; Wei, D.; Zhang, J.; Li, Q.; Yao, R.; Wu, X.; Wang, Y. Optimized groundwater quality evaluation using unsupervised machine learning, game theory and Monte-Carlo simulation. *J. Environ. Manag.* **2024**, *371*, 122902. [CrossRef] [PubMed]
66. Othman, F.; Farrag, A.; Mohamed, A.M.; Seleem, E.-M.M.; Salman, S.A. Groundwater Quality Evaluation Using Hydrogeochemical and GIS Techniques in the Southwest Part of Sohag, Egypt. *Iraqi Geol. J.* **2022**, *55*, 93–104. [CrossRef]
67. Loganathan, S.; Sathiyamoorthy, M. Groundwater quality assessment for drinking, irrigation purposes and fuzzy logic-based water quality index for industrial suitability in Walajapet taluk, Ranipet district, Tamil Nadu, India. *AQUA—Water Infrastruct. Ecosyst. Soc.* **2024**, *73*, 1766–1787. [CrossRef]
68. Elnazer, A.A.; Seleem, E.-M.M.; Zeid, S.A.M.; Ismail, I.S.A.; Bahlol, H.A.; Salman, S.A. Hydrochemical evaluation of the quaternary aquifer and its suitability for different purposes at south Al Waqf city, Qena, Upper Egypt. *Groundw. Sustain. Dev.* **2021**, *12*, 100517. [CrossRef]
69. Kumar, R.; Sharma, S.; Prashant, M. Assessment of groundwater quality for drinking, irrigation and industrial purposes in Aik Watershed, Jammu and Kashmir, India. *Discov. Geosci.* **2024**, *2*, 58. [CrossRef]
70. He, Q.; Li, P.; Wang, Y.; He, X.; Fida, M.; Elumalai, V. Hydrochemical characteristics of groundwater and their controlling mechanisms in irrigation and non-irrigation areas—A comparative study in the Guanzhong Plain of China. *Phys. Chem. Earth Parts A/B/C* **2024**, *136*, 103781. [CrossRef]
71. Xiao, Y.; Liu, K.; Hao, Q.; Xiao, D.; Zhu, Y.; Yin, S.; Zhang, Y. Hydrogeochemical insights into the signatures, genesis and sustainable perspective of nitrate enriched groundwater in the piedmont of Hutuo watershed, China. *CATENA* **2022**, *212*, 106020. [CrossRef]
72. Wang, D.; Li, P.; Yang, N.; Yang, C.; Zhou, Y.; Li, J. Distribution, sources and main controlling factors of nitrate in a typical intensive agricultural region, northwestern China: Vertical profile perspectives. *Environ. Res.* **2023**, *237*, 116911. [CrossRef]
73. Alam, S.M.K.; Li, P.; Fida, M. Groundwater Nitrate Pollution Due to Excessive Use of N-Fertilizers in Rural Areas of Bangladesh: Pollution Status, Health Risk, Source Contribution, and Future Impacts. *Expo. Health* **2024**, *16*, 159–182. [CrossRef]
74. Orellana-Macías, J.M.; Perles Roselló, M.J.; Causapé, J. A Methodology for Assessing Groundwater Pollution Hazard by Nitrates from Agricultural Sources: Application to the Gallocanta Groundwater Basin (Spain). *Sustainability* **2021**, *13*, 6321. [CrossRef]
75. Rahman, A.; Mondal, N.C.; Tiwari, K.K. Anthropogenic nitrate in groundwater and its health risks in the view of background concentration in a semi arid area of Rajasthan, India. *Sci. Rep.* **2021**, *11*, 9279. [CrossRef] [PubMed]
76. Raheem, A.; Ahmad, I.; Arshad, A.; Liu, J.; Rehman, Z.U.; Shafeeque, M.; Rahman, M.M.; Saifullah, M.; Iqbal, U. Numerical Modeling of Groundwater Dynamics and Management Strategies for the Sustainable Groundwater Development in Water-Scarce Agricultural Region of Punjab, Pakistan. *Water* **2024**, *16*, 34. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.