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Spatial Variations and Regulating Processes of Groundwater Geochemistry in an Urbanized Valley Basin on Tibetan Plateau

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Abstract: Groundwater resource is crucial for the development of agriculture and urban communities in valley basins of arid and semiarid regions. This research investigated the groundwater chemistry of a typical urbanized valley basin on the Tibetan Plateau to understand the hydrochemical status, quality, and controlling mechanisms of groundwater in arid urbanized valley basins. The results show groundwater is predominantly fresh and slightly alkaline across the basin, with approximately 54.17% of HCO_3-Ca type. About 12.5% and 33.33% of sampled groundwaters are with the hydrochemical facies of Cl-Mg·Ca type and Cl-Na type, respectively. Groundwater is found with the maximum TDS, NO_3^-, NO_2^-, and F^- content of 3066 mg/L, 69.33 mg/L, 0.04 mg/L, and 3.12 mg/L, respectively. Groundwater quality is suitable for domestic usage at all sampling sites based on EWQI assessment but should avoid direct drinking at some sporadic sites in the urban area. The exceeding nitrogen and fluoride contaminants would pose potential health hazards to local residents, but high risks only existed for infants. Both minors and adults are at medium risk of these exceedingly toxic contaminants. Groundwater quality of predominant sites in the basin is suitable for long-term irrigation according to the single indicator of EC, SAR, %Na, RSC, KR, PI, and PS and integrated irrigation quality assessment of USSL, Wilcox, and Doneen diagram assessment. But sodium hazard, alkalinity hazard, and permeability problem should be a concern in the middle-lower stream areas. Groundwater chemistry in the basin is predominantly governed by water-rock interaction (silicate dissolution) across the basin in natural and sporadically by evaporation. Human activities have posed disturbances to groundwater chemistry and inputted nitrogen, fluoride, and salinity into groundwater. The elevated nitrogen contaminants in groundwater are from both agricultural activities and municipal sewage. While the elevated fluoride and salinity in groundwater are only associated with municipal sewage. It is imperative to address the potential anthropogenic contaminants to safeguard groundwater resources from the adverse external impacts of human settlements within these urbanized valley basins.

Keywords: hydrochemistry; groundwater resource; water quality assessment; agricultural pollution; urbanization

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1. Introduction

Urbanization has emerged as one of the most significant trends of the 21st century, and more than half of the global population resides in urban areas nowadays [1–3]. The sustainable development of urban environments is inextricably linked to a stable and reliable supply of freshwater resources, which are essential not only for the prosperity of

agriculture and industry but also for economic growth and the maintenance of healthy ecosystems [3–5]. Thus, research on the availability of freshwater resources is crucial for the development of natural systems and the human community.

Groundwater is widely acknowledged as a preferred water supply source due to its wide distribution, low pollution, steady flow, and quality [6]. Globally, it provides drinking water for billions of people and supports a wide range of economic activities, including agriculture and industry [7–9]. With the rapid urbanization taking place across many regions, ensuring an adequate supply of high-quality groundwater is more and more essential for socioeconomic development. However, it should be realized that groundwater resources are also facing threats from continuous global population growth, accelerated urbanization, and intensified climate change impacts, bringing mounting challenges for sustainable groundwater utilization [10–12]. The availability of groundwater depends not only on quantity but also on quality [13]. Therefore, groundwater chemistry and quality assessments are of paramount importance to provide the necessary scientific foundation for creating management strategies to safeguard groundwater and ensure its sustainable use in urbanized regions [14–16].

Normally, groundwater chemistry is the result of various natural factors, such as recharge water property, lithology of aquifers, and evaporation intensity [17–19]. Human activities have played an increasingly significant role in influencing the groundwater components over the past decades, resulting in heavy salinization and pollution of groundwater [20–22]. Plenty of studies have indicated the serious negative impacts that groundwater degradation has on human survival and ecosystem balance [23–25]. In agriculture, the use of highly saline groundwater for irrigation operations will be harmful to both soil and plants, leading to adverse consequences such as soil consolidation, decreased fertility, and reduced crop yields [25,26]. In daily water consumption, it is globally acknowledged that nitrate and fluoride are the most common pollutants deteriorating the groundwater quality [27,28]. Generally, anthropogenic inputs are the main factors contributing to excessive nitrate and fluoride in groundwater in comparison with natural processes [27,29,30]. Especially, it is reported that anthropogenic practices such as fertilizer overuse and improper disposal of manure sewage are the main causes of groundwater nitrate contamination [31–33]. Apparently, understanding groundwater chemistry means clarifying the specific processes of natural and anthropogenic factors that regulate groundwater geochemistry [34].

As serious groundwater pollution becomes prevalent, the corresponding health problem has been a concern for drinking in many regions [14,35]. Reportedly, drinking groundwater with surplus nitrate could lead to human diseases, including cardiovascular disease and blue baby syndrome [12,36]. Also, over intake of fluoride through groundwater could damage human health with the diseases of dental fluorosis and skeletal fluorosis [37,38]. A number of studies have investigated the human health risks associated with groundwater pollutants, donating significantly to the healthy groundwater supply around the world [39–45]. However, still inadequate attention has been paid to the valley basins in arid and semi-arid regions [46].

Valley basins are important landform units for human settlement in arid and semi-arid regions, besides alluvial fan plains. Owing to the flat terrain and convenient water sources, there have developed different scales of urban in the valley basins of arid and semi-arid regions. Although the river across the valley could ensure a certain domestic water supply, the arid climate with limited precipitation and strong evaporation makes significantly unstable changes in river water flow and quality, which leaves the uncertainty of a prolongedly reliable and sustainable water supply. As a result, groundwater is considered as the ideal water source for various usages in the arid valley basins, thereby highlighting the necessity of comprehensive knowledge regarding groundwater chemistry and its suitability to achieve sustainable development in urbanized valley basins of arid and semi-arid regions.

This study aims to reveal the hydrochemical characteristics, quality, and genesis of groundwater in the urbanized valley basins of arid and semiarid regions, with the example of the Beichuan River Basin on the Tibetan Plateau. The specific goals of this study are: (1) to identify the spatial distinction of groundwater hydrochemical characteristics; (2) to evaluate the groundwater quality for various usages and potential human health risks; and (3) to elucidate the dominant mechanisms governing the groundwater geochemistry. The findings of this study could be beneficial for the effective management and utilization of groundwater for sustainable purposes in arid valley basins under urbanization.

2. Description of Study Area

The Beichuan River basin, a typical urbanized valley basin, is located in the northern part of the Huangshui River basin (Figure 1). The area is defined by the coordinates ranging from 101°7′7″ E to 101°54′11″ E for longitude, and from 36°38′33″ N to 37°14′17″ N for latitude, covering a total area of 194.28 km^2. The basin exhibits a slender, elongated form, encircled by mountains on three sides, and has a central valley plain. The region's altitude ranges from 2215 m to 4375 m. The Huangshui River's first-level tributary, the Beichuan River, runs through the entire basin from north to south. This area has a semi-arid plateau continental climate. The average annual temperature is 5.8 °C, the highest temperature is 15.0 °C, and the lowest temperature is −12.0 °C. The annual precipitation reaches 512.8 mm, with most of the rainfall concentrated in June to September, accounting for about 70% of the yearly precipitation. The annual evaporation amount is 1426.4 mm, nearly three times the rainfall, indicating a high likelihood of drought risk in the basin [47].

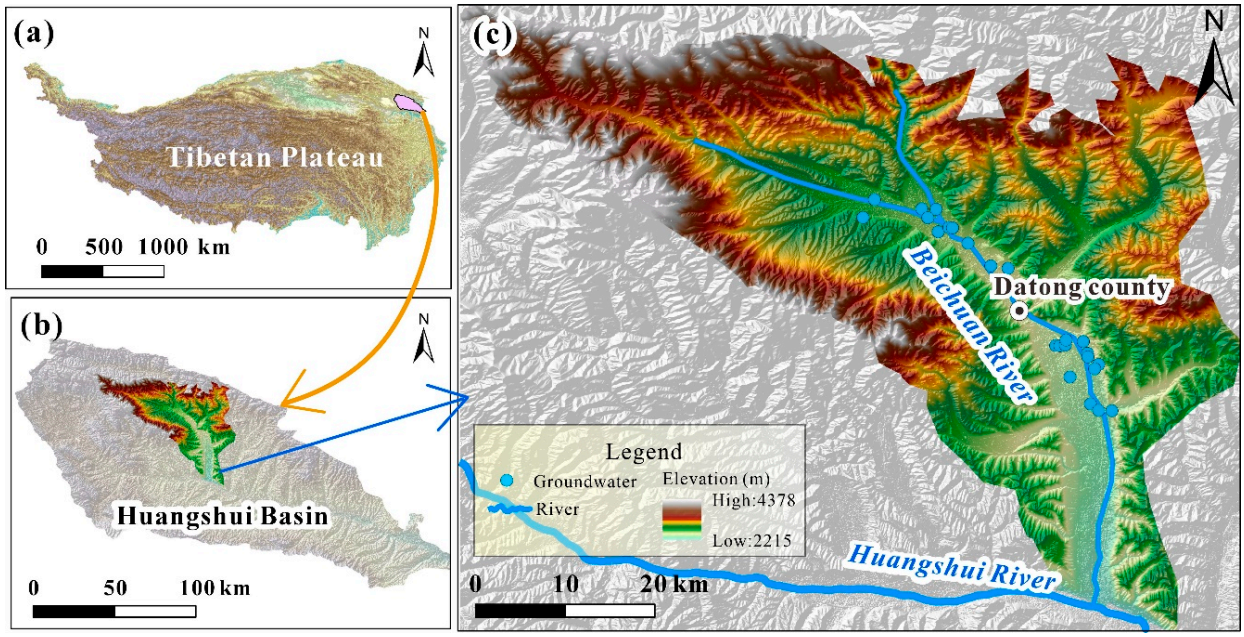


Figure 1. Location of the (**a**) Huangshui Basin, (**b**) the Beichuan River basin, and (**c**) groundwater sampling site within the basin.

Hydrogeologically, the aquifer system of the basin is mainly composed of two parts. On one hand, there is the porous water of the loose rock types in the central valley plain. On the other hand, there is the phreatic water of the loess and underlying gravel in the hills and gullies of the surrounding mountainous areas, as well as the fissured-porous water of the clastic rocks [48]. Overall, the basin is rich in groundwater resources with aquifers that exhibit good hydraulic properties. The well yield of the aquifers in the valley plain exceeds 100 m^3/day for individual wells. In areas along the Middle and lower reaches of the Beichuan River where surface water replenishes groundwater, the well yield can even exceed 5000 m^3/d. In the surrounding mountainous areas, the well yield of the aquifers

also surpasses 8.64 m^3/d for individual wells. Abundant groundwater resources play an irreplaceable role in supplying water to local residents, especially during drier periods.

In recent years, as urbanization in the basin has intensified, both the quantity and quality of local groundwater have faced unprecedented challenges. The advancement of urbanization signifies an increase in population and a rise in water usage for industrial and agricultural purposes [49]. This poses significant pressure on the exploitation of groundwater in the region. Additionally, there is a certain degree of mutual conversion between local groundwater and surface water. This leads to the threat of various industrial and agricultural pollutants to groundwater as well.

3. Materials and Methods

3.1. Sample Collection and Analysis

A total of 24 groundwater samples were collected from the valley basin, all of which were phreatic water extracted from the Borehole well. The samples were primarily concentrated in two areas. One is the agricultural activity area in the upper reaches of the Beichuan River, and the other is the urban area in the middle and lower reaches. These samples are representative of the status of groundwater under two main land use types in the basin. All sampling wells were pumped for more than 15 min to eliminate the influence of standing water in the wells. Before sampling, in-situ measurements of parameters (pH, etc.) were conducted at all sites. All collected groundwater samples were stored in high-density polyethylene bottles that had been pre-rinsed 3 to 5 times with the target groundwater. The collected samples were kept at a temperature of 4 °C and delivered to the laboratory for analysis within 48 h.

The in situ physicochemical parameters (HACH HQ4D, Loveland, CO, USA) were measured using portable meters. The detection of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) was performed using an inductively coupled plasma mass spectrometer (Agilent 7500ce ICP-MS, Tokyo, Japan). Ion chromatography (Shimadzu LC-10ADVP, Kyoto, Japan) was employed for the detection of major anions ($SO_4{}^{2-}$, Cl^-, $NO_3{}^-$, F^-) and $NH_4{}^+$. The determination of $HCO_3{}^-$ was carried out using acid-base titration. TDS was measured by the gravimetric analysis method. According to previous work, heavy metals have been reported detected in the water system of the basin [50]. Therefore, the trace elements and heavy metals are also measured in the present research with the aid of inductively coupled plasma spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan). To ensure the accuracy of the analytical results, each groundwater sample was subjected to three replicate tests. The standard and blank controls are interspersed throughout the experimental process. The ionic charge balance error percentage of the water sample test results was within ±5%, indicating that the test results are reliable.

3.2. Entropy Water Quality Index (EWQI)

EWQI is an effective method to quantitatively appraise the groundwater drinking quality. It is information entropy-based so it could avoid the subjective weights given by experts in the traditional assessing method. Hence, EWQI has been widely adopted in studies on groundwater quality due to its more objective idea. It calculates the groundwater drinking quality using the hydrochemical parameters. The calculation procedure of EWQI usually follows the steps of creating an eigenvalue matrix, standardizing the eigenvalue matrix, calculating the information entropy and entropy weight, and quantifying the EWQI results, specifically listed as the following Equations (1)–(8):

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

$$y_{ij} = \frac{x_{ij} - (x_{ij})_{min}}{(x_{ij})_{max} - (x_{ij})_{min}} \tag{2}$$

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

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^{m} y_{ij}} \tag{4}$$

$$e_j = -\frac{1}{\ln m} \sum_{i=1}^{m} (P_{ij} \times \ln P_{ij}) \tag{5}$$

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

$$q_j = \frac{C_j}{S_j} \times 100 \tag{7}$$

$$EWQI = \sum_{j=1}^{m} (w_j \times q_j) \tag{8}$$

where X is the eigenvalue matrix, Y is the standardized matrix, m represents the groundwater sample amount, n represents the hydrochemical parameter amount, P_{ij} denotes the probability of different parameters, e_j denotes the information entropy, w_j signifies the entropy weight, and q_j signifies the quality rating scale of different parameters.

3.3. Human Health Risk Assessment (HHRA)

The HHRA model developed by the United States Environmental Protection Agency (USEPA) is employed in this study to ascertain the potential health risks to the public. This is a practical means that benefits safe groundwater supply. This method combines contaminants with human health and gives a quantitative characterization of the impacts on human health from exposure to polluted groundwater. In general, there are various exposure pathways through which the polluted groundwater damages human health, with oral intake and dermal contact being the most common. In consequence, this study estimates the potential human health risks from groundwater pollutants via such two main exposure pathways. Additionally, this study considers physiological differences to divide the populations into four groups: infants, children, adult females, and adult males. The potential health risks of pollutants to humans in the HHRA model are determined as follows:

$$HQ = \frac{CDI}{RfD} \tag{9}$$

$$HI = \sum_{i=1}^{n} HQ_i \tag{10}$$

where CDI represents the chronic daily intake dose of a specific pollutant (mg/kg/day), RfD is the reference dose for a specific pollutant, HQ_i denotes the hazard quotient of the ith pollutant (dimensionless), and HI is the health risk index (dimensionless). For different

exposure pathways, the calculation of *CDI* would also be distinct, and the *CDI* through oral and dermal exposure pathways can be obtained as following equations:

$$CDI_{oral} = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \quad (11)$$

$$CDI_{dermal} = \frac{C_i \times K_p \times SA \times T \times EF \times ED \times EV \times CF}{BW \times AT} \quad (12)$$

where C_i signifies the pollutant concentration (mg/L), *IR* signifies the average drinking rate (L/d), *EF* is the exposure frequency (d/a), *ED* is the exposure duration (a), BW indicates the body weight (kg), *AT* indicates the average time (d), K_p denotes skin permeability coefficient (cm/h), *SA* denotes the skin contact surface area (cm^2), *T* is the contact duration (h/d), *EV* indicates the average frequency of dermal contact (time/day), and CF indicates unit conversion factor (L/cm^3). The values of the aforementioned parameters used in this study are given in Table 1, reference from the existing studies [14].

Table 1. Exposure parameters used in the HHRA model for different populations in the study area.

Exposure Parameter	Infants	Children	Females	Males
IR	0.65	1.50	2.66	3.72
EF	365	365	365	365
ED	0.5	6	30	30
BW	6.94	25.9	64	73
AT	365 × ED	365 × ED	365 × ED	365 × ED
K_p	0.001	0.001	0.001	0.001
SA	3640	9186	17,166	18,482
T	0.4	0.4	0.4	0.4
EV	1	1	1	1
CF	0.002	0.002	0.002	0.002
RfD_{oral}-NO_3^-	1.6	1.6	1.6	1.6
RfD_{dermal}-NO_3^-	0.8	0.8	0.8	0.8
RfD_{oral}-F^-	0.06	0.06	0.06	0.06
RfD_{dermal}-F^-	0.03	0.03	0.03	0.03

3.4. Groundwater Irrigation Quality Indices

Since agricultural practice is an essential activity in the northern Beichuan River Basin, it is necessary to consider a series of groundwater irrigation quality indices to evaluate the groundwater suitability for irrigation usage. The indices involved in this study are separately electrical conductivity (EC in μS/cm), sodium adsorption ratio (*SAR*), sodium percent (%Na), residual sodium carbonate (*RSC*), Kelly's ratio (*KR*), permeability index (*PI*), and potential salinity (*PS*). The calculation methods for these parameters are provided below [25]:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \quad (13)$$

$$\%Na = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \quad (14)$$

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (15)$$

$$KR = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \quad (16)$$

$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100 \quad (17)$$

$$PS = Cl^- + \frac{1}{2}SO_4^{2-} \quad (18)$$

where the concentrations of all ions above are in units of meq/L. The evaluation standards of groundwater irrigation quality in view of the calculated indices are exhibited in the subsequent sections in detail.

Besides, the combination of certain irrigation indices provides a comprehensive interpretation of the groundwater irrigation quality [9,16], for example, the permeability index diagram using the PI versus total ion concentration (meq/L), the Wilcox diagram consisting of EC and %Na, and the USSL diagram constructed by SAR and salinity hazard.

4. Results and Discussion

4.1. Statistical Analysis of Groundwater Hydrochemistry

The hydrochemical parameters of groundwater sampled from the Beichuan River basin are statistically presented in Table 2. The table also includes the drinking water standards recommended by the World Health Organization [51] and Chinese guidelines [52] for comparative analysis. The groundwater samples exhibit a slightly alkaline character, with pH values ranging from 7.13 to 8.31 and a mean pH of 7.59. Groundwater in the Beichuan River basin displays a broad spectrum of Total Dissolved Solids (TDS) and Total Hardness (TH) concentrations, with TDS ranging from 206.00 to 3066.00 mg/L and TH from 32.60 to 866.00 mg/L. High TDS levels in drinking water can cause kidney damage and soil salinization, in addition to restricting its use for both consumption and industrial purposes. Thus, attention should be paid to the high TDS groundwater. However, the majority of the groundwater samples exhibit low Total Hardness (TH) levels, with only 4.17% surpassing the threshold stipulated by the Chinese guidelines [52]. While 29.17% of the groundwater samples with Total Dissolved Solids (TDS) exceeding the 1000 mg/L threshold are categorized as brackish or saline water. The spatial distribution of Total Dissolved Solids (TDS) reveals that the majority of brackish or saline groundwaters are concentrated in the downstream region of the basin (Figure 2). Furthermore, a progressive increase in salinity is observed in groundwater as one moves from the upstream to the downstream areas.

Table 2. Statistical summary of groundwater hydrochemical composition within the basin.

Index	Unit	Min	Max	Mean	SD *	Guideline	% of the Sample Exceeding the Guideline
pH	/	7.13	8.31	7.59	0.29	6.5–8.5 **	/
TDS	mg/L	206.00	3066.00	824.50	770.05	1000 **	29.17%
TH	mg/L	32.60	866.00	171.75	176.03	450 **	4.17%
K^+	mg/L	1.41	13.04	4.13	2.66	/	/
Na^+	mg/L	10.82	1132.00	176.90	274.03	200 **	25.00%
Ca^{2+}	mg/L	45.11	154.60	86.51	30.20	75 ***	58.33%
Mg^{2+}	mg/L	7.45	88.00	23.96	18.80	50 ***	8.33%
Cl^-	mg/L	6.40	1283.22	160.90	289.18	250 **	16.67%
$SO_4{}^{2-}$	mg/L	42.19	648.38	201.12	195.78	250 **	25.00%
$HCO_3{}^-$	mg/L	136.61	558.00	270.68	113.75	/	/
F	mg/L	0.12	3.32	0.78	0.75	1.0 **	33.33%
$NO_3{}^-$	mg/L	0.06	69.33	26.94	21.75	50.0 ***	20.83%
$NO_2{}^-$	mg/L	0.00	0.04	0.00	0	0.02 **	12.50%

* Standard Deviation; ** Chinese Guideline [52]; *** WHO Guideline [51].

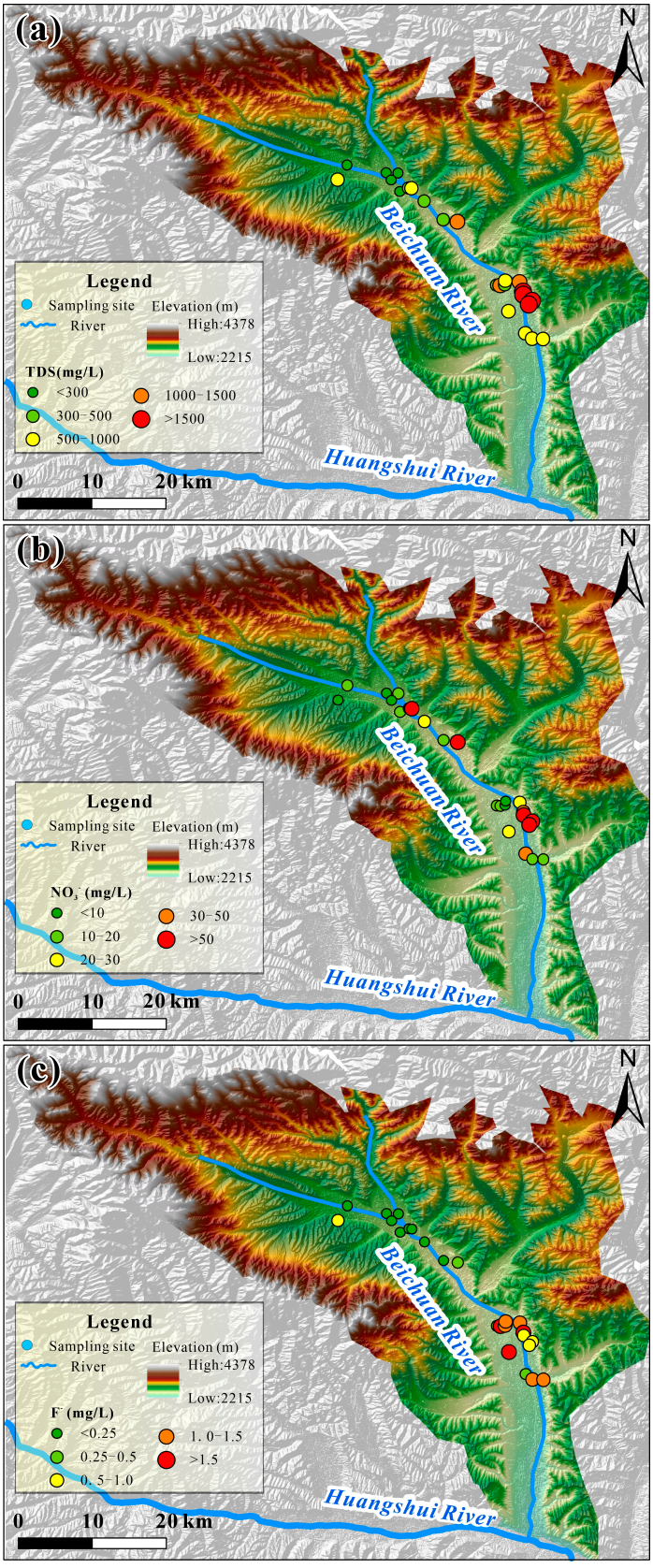


Figure 2. Spatial distribution of (**a**) TDS, (**b**) NO_3^-, and (**c**) F^- content in groundwater within the basin.

In the Beichuan River watershed, the solute chemistry of groundwater is predominantly influenced by the cation Ca^{2+} (Figure 3). The concentration of Ca^{2+} spans from 45.11 mg/L to 154.60 mg/L, with an average concentration of 86.51 mg/L. Na^{+} and Mg^{2+}, as the second and third most abundant cations, exhibit concentration ranges of 10.82 to 1132.00 mg/L and 7.45 to 88.00 mg/L, respectively. Among the cations, K^{+} was detected at the lowest concentrations, with values ranging from 1.41 mg/L to 13.04 mg/L and an average of 4.13 mg/L (Table 2). Among the major anions of groundwater in this region, a clear dominance is observed in the order of $HCO_3^{-} > SO_4^{2-} > Cl^{-}$ (Figure 3). The concentrations of these predominant anions exhibit a broad range (Table 2). The concentration of HCO_3^{-} varies within the range of 136.61 to 558.00 mg/L. SO_4^{2-} and Cl^{-} concentrations span from 42.19 mg/L to 648.38 mg/L and 6.40 mg/L to 1283.22 mg/L, respectively. As illustrated in Figure 3, the hydrochemical composition of groundwater in the Beichuan River basin is predominantly characterized by the HCO_3-Ca type, accounting for 54.17% of the groundwater samples. This is followed by the Cl-Na type, representing 33.33%, and the Mixed Cl-Mg·Ca type, which constitutes 12.5%. With increasing Total Dissolved Solids (TDS), there is a progressive shift in water chemistry from the HCO_3-Ca type to the Cl-Na type. This trend suggests that the hydrochemical evolution of groundwater in the Beichuan River basin transitions from the HCO_3-Ca type to the mixed Cl-Mg·Ca type and finally to the Cl-Na type as one moves from upstream to downstream.

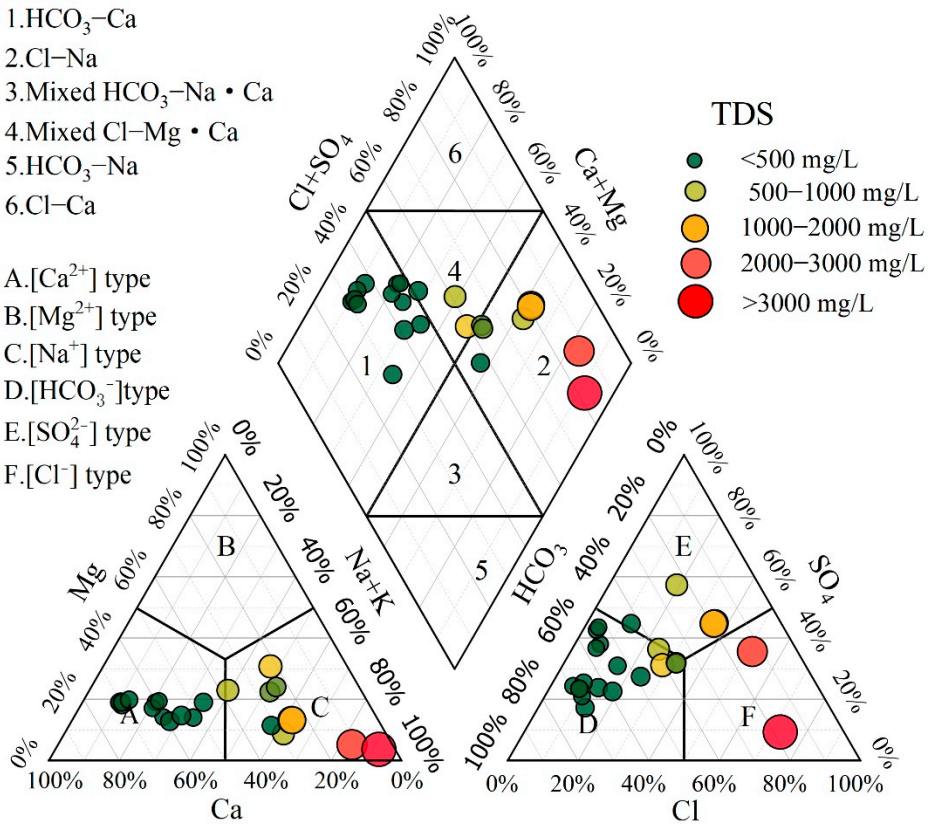


Figure 3. Piper diagram of groundwater regarding different TDS in the Beichuan River watershed.

Trace elements and toxic metals, including nitrogen (N), fluoride (F), iodine (I), arsenic (As), iron (Fe), manganese (Mn), and zinc (Zn), were analyzed for their potential impact on groundwater quality and safety in the Beichuan River basin. The analysis reveals that only the concentrations of NO_3^{-} and NO_2^{-} and F^{-} occasionally surpass the thresholds set by the World Health Organization [51] and Chinese guidelines [52], posing a risk to groundwater quality. Specifically, fluoride concentrations vary from 0.12 mg/L to 3.12 mg/L, with a mean of 0.78 mg/L. Approximately 33.33% of the groundwater samples exceed the Chinese guideline of 1 mg/L for potable water, with these enriched waters predominantly located

in the downstream areas (Figure 2). NO_3^- concentrations range from 0.06 to 69.33 mg/L, averaging 26.94 mg/L, with 20.83% of the samples exceeding the WHO's recommended standard, primarily in the valley regions (Figure 2). This suggests that human activities have impacted groundwater quality to some extent [8]. Additionally, the maximum NO_3^- concentration is 0.04 mg/L, with 12.50% of samples exceeding the drinking water safety limit of 0.02 mg/L. Collectively, these findings underscore the need for vigilance regarding localized nitrogen and fluoride contamination, which could compromise the suitability of groundwater for drinking in the Beichuan River basin (Table 2).

4.2. Water Quality for Various Utilization

4.2.1. Overall Water Quality Based on EWQI

To understand the overall groundwater quality in the basin, the entropy water quality index approach [15] was introduced in the present research. A comprehensive set of 13 hydrochemical parameters was considered in the assessment. The results show that the EWQI values of groundwater span from 26.7 to 143.4, with a mean of 64.05 (Figure 4a). The distribution of groundwater quality is as follows: 50% falls within Rank 1, 33.3% within Rank 2, and 16.7% within Rank 3. Collectively, 83.3% of the groundwater samples are deemed suitable for drinking, suggesting that the overall groundwater quality in the basin is relatively good. Additionally, a positive correlation was observed between the EWQI and TDS, implying that TDS can serve as an indicative measure of groundwater quality to a certain extent.

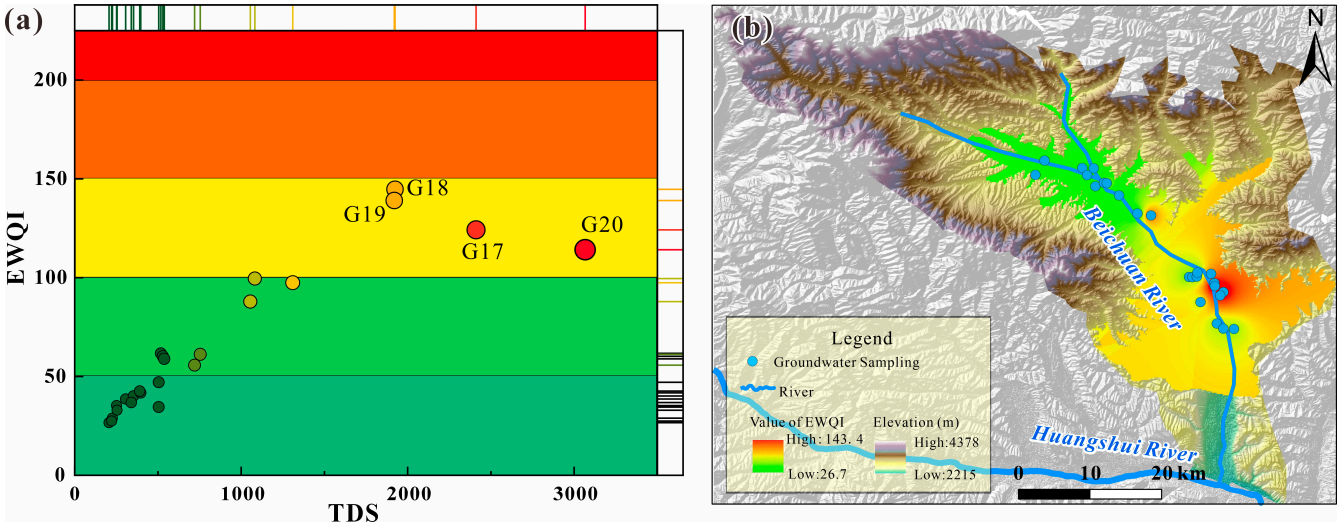


Figure 4. (**a**) Scatterplot of EWQI versus TDS, and (**b**) the spatial interpolation graph of EWQI of groundwater within the basin.

The spatial distribution of the EWQI value indicates that groundwater with superior quality is predominantly found in the upper reaches of the basin (Figure 4b). This pattern is attributed to the fact that upstream groundwater sources are primarily recharged by precipitation, meltwater from snow and ice, and seepage from rivers, occurring in regions where human activities are minimal. Conversely, the downstream areas show a notable degradation in groundwater quality, with some areas no longer meeting the criteria for potable water. Consequently, residents in the downstream regions of the basin should exercise caution when considering the use of local groundwater as a direct source of drinking water, due to potential water quality concerns.

4.2.2. Potential Health Threats of Toxic Elements to Humans

In addition to the EWQI, the non-carcinogenic health risks potentially posed by toxic substances also serve as another significant indicator in assessing groundwater quality [53]. In this study, the exceedingly toxic substances, including NO_3^-, NO_2^-, and F^-, may pose

a significantly apparent non-carcinogenic risk to the population in the study area. For example, the excessive nitrogen in drinking water would result in dysfunction of blood transporting oxygen and cancers of the colon and stomach [14,54,55]. When examining the susceptibility of different demographic groups to these substances, it's prudent to categorize the population by age and gender, as this study does, into infants, children, adult males, and adult females [56]. This approach allows for a more nuanced understanding of how various groups may be affected by the presence of these substances in the groundwater. By taking into account the specific vulnerabilities of these groups, more targeted measures can be implemented to mitigate potential health risks and ensure the safety of the groundwater supply.

The results indicate that the average non-carcinogenic health risks of groundwater for infants, children, adult females, and adult males are 2.803, 1.738, 1.240, and 1.555, respectively (Table 3). Infants, due to their inherent vulnerability, exhibit the highest non-carcinogenic health risks, followed by children, adult males, and adult females. For infants and children, a considerable proportion of the population, specifically 62.5% and 66.7%, respectively, are exposed to moderate non-carcinogenic health risks (Figure 5). Furthermore, a significant subset of infants, amounting to 29.2%, are exposed to a high degree of non-carcinogenic risk. Adult males and females are not significantly exposed to high risk; rather, the proportion of those exposed to moderate risk is 58.3% and 66.7%, respectively. In conclusion, the non-cancer risks to infants in the study area are extremely high. Failure to take timely and appropriate action may result in irreversible damage to the health and development of the infant population.

Table 3. The health risk situations of various population groups within the basin.

	Median	Average	Max	Min	Proportion		
					Low Risk	Medium Risk	High Risk
Infants	2.803	2.947	6.255	0.592	8.3%	62.5%	29.2%
Children	1.738	1.831	3.876	0.367	33.3%	66.7%	0.0%
Female	1.240	1.313	2.763	0.263	41.7%	58.3%	0.0%
Male	1.555	1.730	3.411	0.339	33.3%	66.7%	0.0%

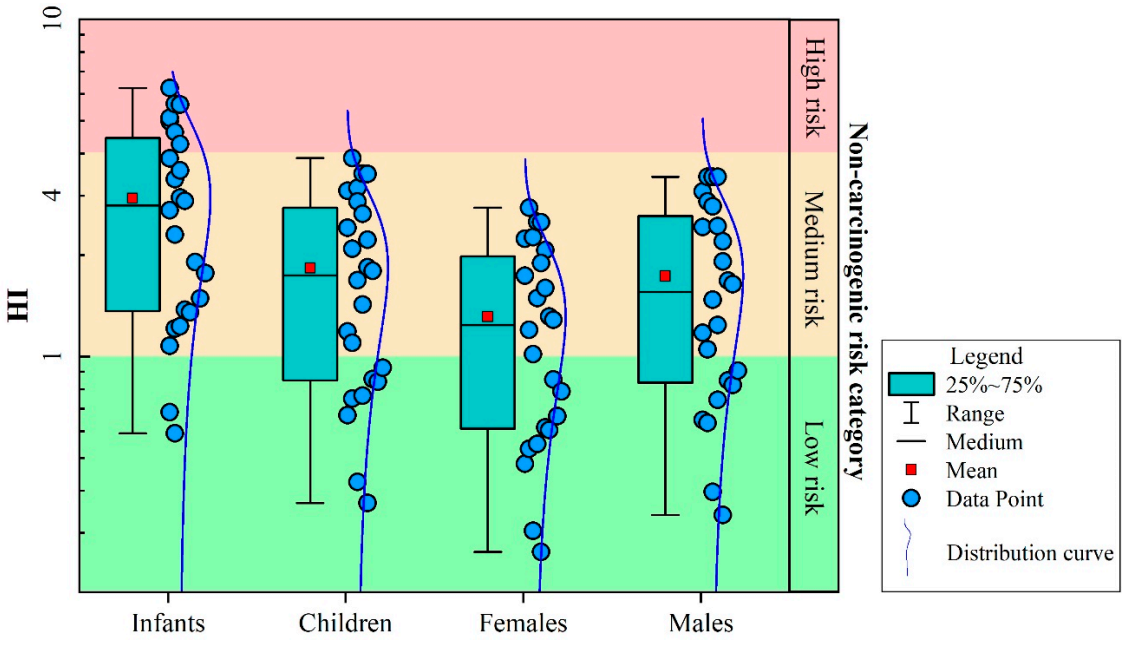


Figure 5. Boxplots of health risks among various population groups within the basin.

The spatial distribution of non-carcinogenic health risks is depicted in Figure 6. It is apparent that the spatial distribution of non-carcinogenic risks closely mirrors the pattern observed in the EWQI distribution. Groundwater in the downstream regions demonstrates elevated non-carcinogenic risks across all age groups. Particularly for infants, groundwater samples with hazard index (HI) values exceeding 3 are predominantly located in the downstream regions of the basin. This distribution pattern is tentatively attributed to the higher population density and concentrated human activities in the downstream areas. The elevated non-carcinogenic risks in groundwater are likely due to the discharge of domestic wastewater and livestock manure, as well as the application of fertilizers. Accordingly, this study suggests implementing tailored water supply strategies for different demographic groups. Furthermore, it is imperative for areas with substantial non-carcinogenic risks to augment the purification of nitrates and fluorides in groundwater, thereby fundamentally mitigating these health hazards.

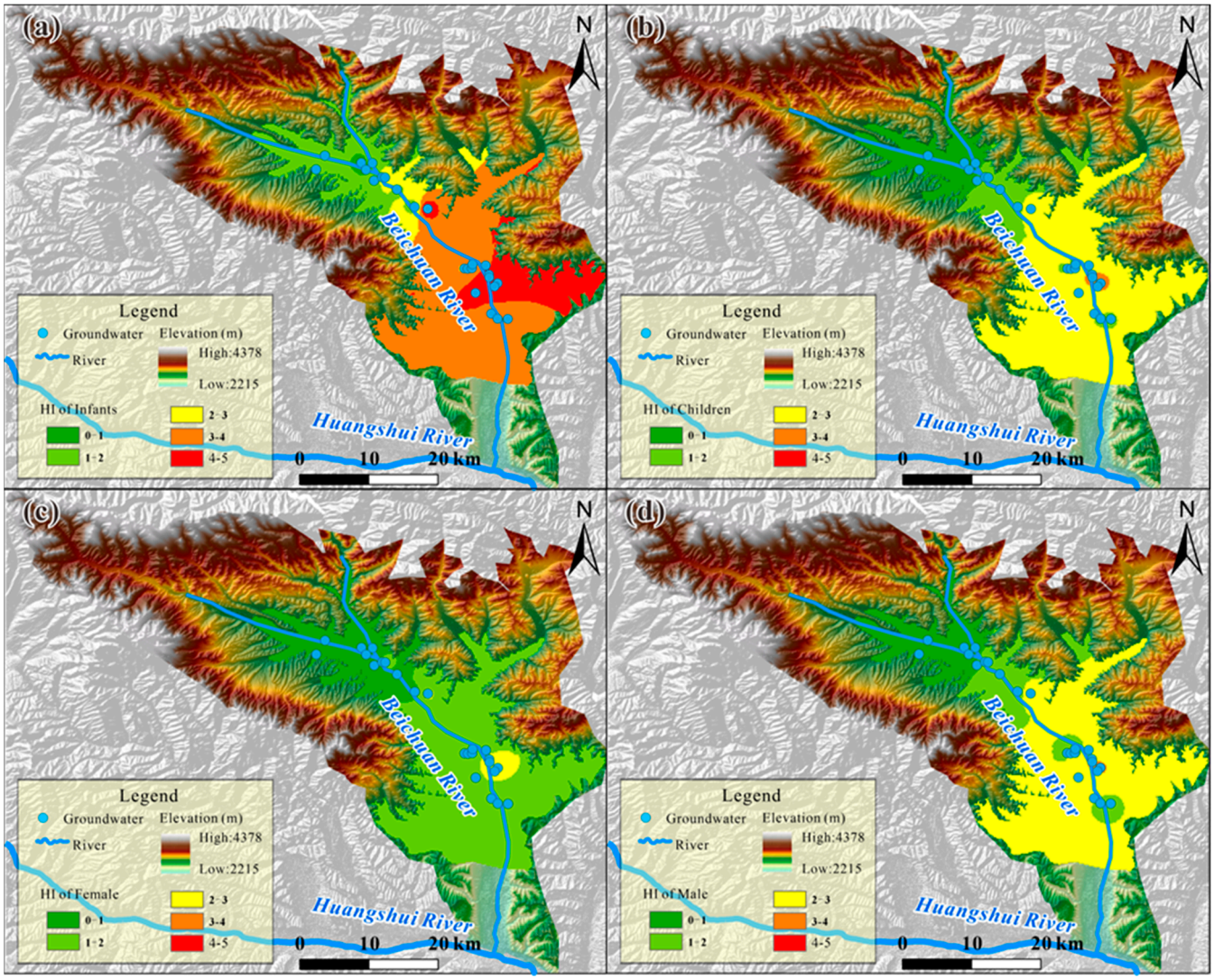


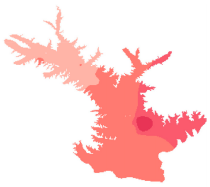
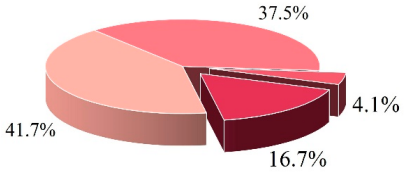
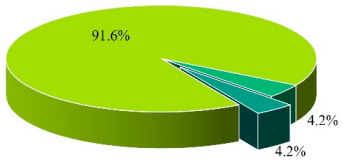
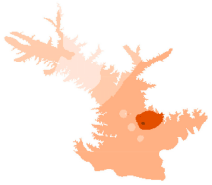
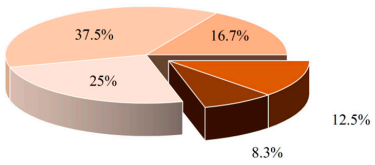
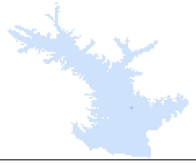
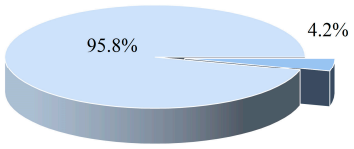
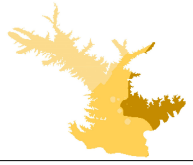
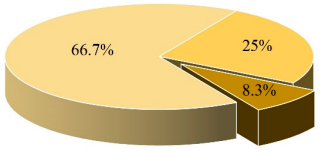
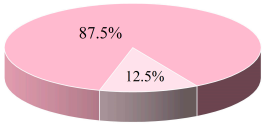
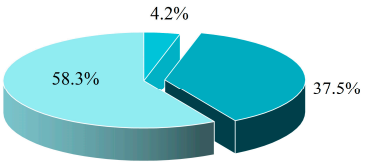
Figure 6. Spatial potential health risks to (**a**) infants, (**b**) children, (**c**) adult females, and (**d**) adult males in the basin.

4.2.3. Water Quality for Sustainable Agricultural Irrigation

Agriculture is one of the most crucial pillar industries in the study area. As the primary source of irrigation water, the quality of phreatic groundwater is vital for agricultural production safety and sustainability [57]. Assessing groundwater quality relies on key indicators such as EC, SAR, %Na, RSC, KR, PI, and PS (Table 4), which are based on various

hydrochemical components [58,59]. Additionally, a comprehensive graphical analysis is also employed in this study to evaluate the overall quality of irrigation water.

Table 4. Classification and spatial distributions of groundwater samples based on irrigation indicators.

Parameters	Range	Category	Proportion	Maps	Graph
EC (µs/cm)	<250	Excellent	0		
	250–750	Good	41.7%		
	750–2000	Permissible	37.5%		
	2000–3000	Doubtful	4.1%		
	>3000	Unsuitable	16.7%		
SAR	<10	Excellent	91.6%		
	10–18	Good	0		
	18–26	Permissible	4.2%		
	>26	Doubtful	4.2%		
Na%	<20	Excellent	25.0%		
	20–40	Good	37.5%		
	40–60	Permissible	16.7%		
	60–80	Doubtful	12.5%		
	>80	Unsuitable	8.3%		
RSC	<1.25	Safe	95.8%		
	1.25–2.5	Doubtful	0		
	>2.5	Unsuitable	4.2%		
KR	<1	Suitable	66.7%		
	1–2	Marginal Suitable	25.0%		
	>2	Unsuitable	8.3%		
PI	>75	Good	12.5%		
	25–75	Suitable	87.5%		
	<25	Unsuitable	0		
PS	<3	Excellent to good	58.3%		
	3–5	Good to injurious	4.2%		
	>5	Injurious to unsatisfactory	37.5%		

The application of saline water in irrigation impairs crop development and diminishes agricultural output. Additionally, high salinity in irrigation water can lead to soil salinization, which indirectly affects crop growth. Electrical conductivity (EC) can be used to infer the total concentration of charged substances in water and serves as an indicator of the irrigation water salinity impact on crops. The values of EC that are below 250 µS/cm or between 250 µS/cm and 750 µS/cm are considered suitable for irrigation and do not adversely affect crops. The EC range of 750 µS/cm to 2000 µS/cm is regarded as moderate

for irrigation purposes. Nonetheless, the EC value greater than 2000 μS/cm is considered inappropriate for irrigation, with levels exceeding 3000 μS/cm having severe negative effects on crop growth, rendering the water unusable for irrigation. In the study area, there is significant variability in EC values of groundwater. Approximately 41.7% of groundwater samples are suitable for irrigation, and 37.5% are acceptable for use in irrigation. Conversely, 20.8% of groundwater samples are unsuitable for irrigation, with most EC values exceeding 3000 μS/cm among them, indicating a high risk of poor irrigation water quality. Spatially, groundwater salinity increases from north to south, with areas of high EC values and samples predominantly concentrated in the southeastern region.

In addition to EC, six other indicators for irrigation water quality assessment were also evaluated in the study area. Most of the samples in the study area had SAR values below 10, classifying them as excellent. However, it is noteworthy that 4.2% of the samples exhibited significantly high SAR values, placing them in the doubtful category, and these samples were concentrated in a small area in the eastern part of the study area. The %Na, a crucial indicator for irrigation water quality, reflects the sodium-alkali content of groundwater. The %Na values of groundwater in the study area varied significantly, with the categories being distributed as follows: 25.0% excellent, 37.5% good, 16.7% permissible, 12.5% doubtful, and 8.3% unsuitable. Spatially, areas with lower %Na values were located in the central and northern parts of the study area, while higher values were concentrated in the southeastern region. RSC, related to the bicarbonate and Ca^{2+} and Mg^{2+} content in water, indicates the ability of irrigation water to reduce free calcium and magnesium. Only one point in the study area fell into the unsuitable range, with the remaining samples being within the safe range. Spatially, the impact of unsuitable samples was limited. KR, first introduced by Kelly, is considered lower values more suitable for irrigation. In the study area, 66.7% of the samples had KR values below 1, making them suitable for irrigation, whereas 8% of the samples had KR values above 2, indicating that they should not be used for irrigation. PI reflects the impact of high concentrations of Na^{+} and HCO_3^{-} in irrigation water on soil. In the study area, 12.5% of the samples had PI values above 75, classifying them as good for irrigation, while the remaining 72.5% of groundwater samples fell between 25 and 75 and were also suitable for irrigation. Spatially, areas with appropriate PI values for irrigation were found in the northeastern part of the study area. From the PS values, 37.5% of the samples posed a significant risk and should be used with caution. Spatially, samples in the central-northern region were classified as Excellent to Good or Good to Injurious, while almost all samples in the southern region fell into the Injurious to Unsatisfactory category, indicating a severe threat to irrigation water quality.

In addition to single-indicator assessments, multi-indicator irrigation quality diagrams are also used to reflect the suitability of irrigation for phreatic groundwater. In this study, three diagrammatic methods, the United States Salinity Laboratory (USSL) diagram, the Wilcox diagram, and the Doneen diagram, are employed to evaluate the holistic water quality [60]. The USSL diagram, first introduced by the United States Salinity Laboratory, evaluates water quality based on the values of groundwater EC and SAR. Groundwater samples are categorized into sixteen sub-classes based on different levels of EC and SAR. As shown in Figure 7a, most samples fall within the low salinity range (S1), with one sample in the moderate salinity range (S2) and two in the very high salinity range (S4). In terms of EC, most samples are in the moderate to high range (C2–C3), with three samples in the extremely high conductivity zone (C4). Overall, three samples in the C4S2 and C4S4 regions exhibit very high irrigation risk, while a part of the sample in the C3S1 region also shows a higher irrigation water quality risk. Samples in the C2S1 region display relatively better irrigation water quality.

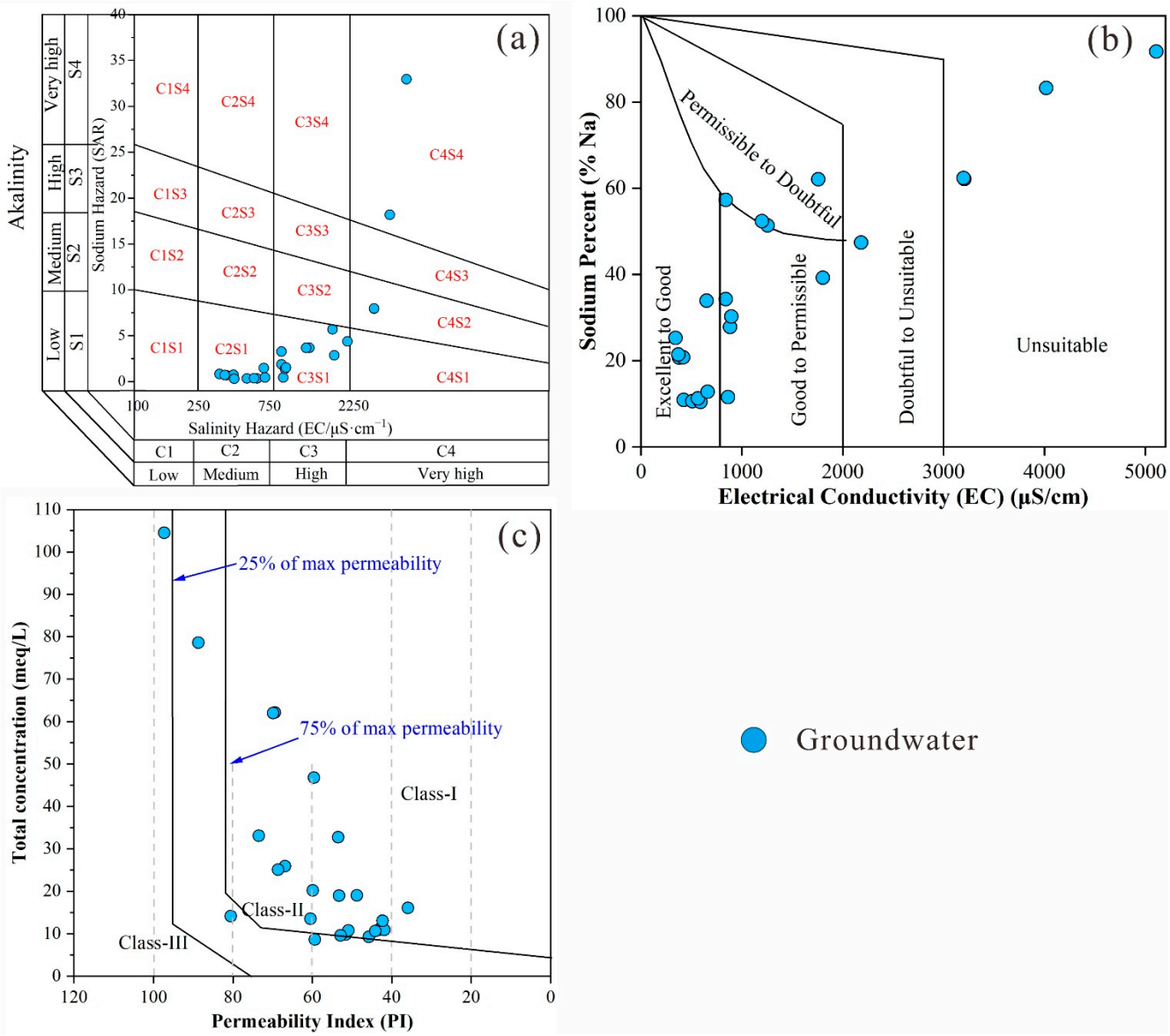


Figure 7. The irrigation water quality demonstrated by (**a**) USSL diagram, (**b**) Wilcox diagram, and (**c**) Doneen diagram.

The Wilcox diagram divides water samples into five categories based on EC and Na%, reflecting their usability for irrigation. There is significant variability in water quality across the study area, with samples distributed across each different category (Figure 7b). The proportions of the five categories, including Excellent to Good, Good to Permissible, Permissible to Doubtful, Doubtful to Unsuitable and Unsuitable, are 41.67%, 25.0%, 12.5%, 4.16%, and 16.67%, respectively. According to the Wilcox diagram, 66.67% of the samples are suitable for irrigation, while 8% have questionable usability, indicating potential sodium hazards when used for irrigation.

The impact of irrigation water quality on soil can be illustrated using Figure 7c. This diagram categorizes water samples into three classes based on total concentration and PI, using 25% and 75% tolerance lines. Most samples fall into Class 1, indicating minimal harm to soil. Three samples are in Class 2, suggesting a moderate risk to soil, while one sample in Class 3 is considered to pose a severe potential irrigation risk to local soil.

4.3. Processes Regulating Groundwater Hydrochemistry Variation

Groundwater hydrochemistry is generally regulated by both natural and anthropogenic processes [61]. Gibbs diagram is considered an effective method for differentiating the dominant processes governing water chemistry in nature [62]. As shown in Figure 8, groundwater sampled from the upper-stream areas is distributed in the rock dominance of the Gibbs diagram. This indicates that the interactions between water and rock are the main natural regulating process of groundwater chemistry. Groundwater samples from the middle and lower reaches are found distributed in the evaporation dominance of the Gibbs diagram (Figure 8), suggesting evaporation plays a dominant role in the natural regulating processes of these groundwaters. Spatially, as one progresses downstream along the Beichuan River, the predominant natural mechanism governing groundwater chemistry in the basin transitions progressively from water-rock interaction to evaporation (Figure 8). Concomitant with the shift in groundwater regulation mechanisms, there is a corresponding alteration in the Total Dissolved Solids (TDS) levels. Groundwater that is predominantly influenced by evaporation exhibits elevated Total Dissolved Solids (TDS) concentrations. These groundwaters are found located in the middle and lower stream areas where, with more densely human activities, as a result, are also more vulnerable to anthropogenic impacts.

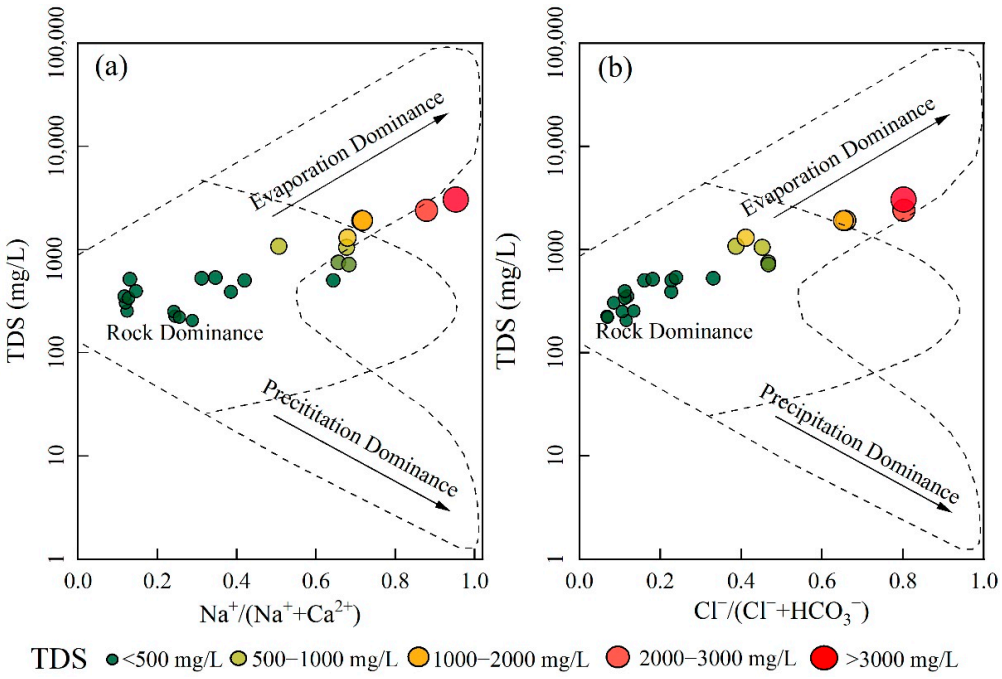


Figure 8. The Gibbs diagram of (**a**) TDS versus $Na^+/(Na^+ + Ca^{2+})$ and (**b**) TDS versus $Cl^-/(Cl^+ + HCO_3^-)$ of groundwater within the basin.

To further refine the natural mechanisms regulating groundwater chemistry in the basin, the end-member diagram is introduced for description [63]. Previous research has demonstrated the effectiveness of this method. In the basin, groundwater samples are primarily distributed between the evaporites and silicate end-members on the diagram (Figure 9). Groundwater with lower TDS levels in the upper reaches of the Beichuan River is primarily distributed near the silicate end-member (Figure 9). This observation indicates that in the upstream regions, where water-rock interaction predominantly governs the groundwater dynamics, the interaction primarily involves silicate minerals. Additionally (Figure 9), two groundwater samples with high TDS values are found located in the evaporite dominance, implying the contribution of evaporite dissolution to groundwater chemistry. As illustrated in Figure 2a, these high TDS groundwaters are located in the middle lower stream area. Evaporation is also evidenced as the dominant regulation of

groundwater chemistry in these areas (Figure 8). Evaporites could be formed in these sites during the fluctuation of groundwater level and then dissolve into groundwater again under proper circumstances and provide the sources of groundwater chemicals. Overall, groundwater chemical solutes are naturally dominated by the dissolution of silicates, followed by evaporite dissolution at some sporadic sites.

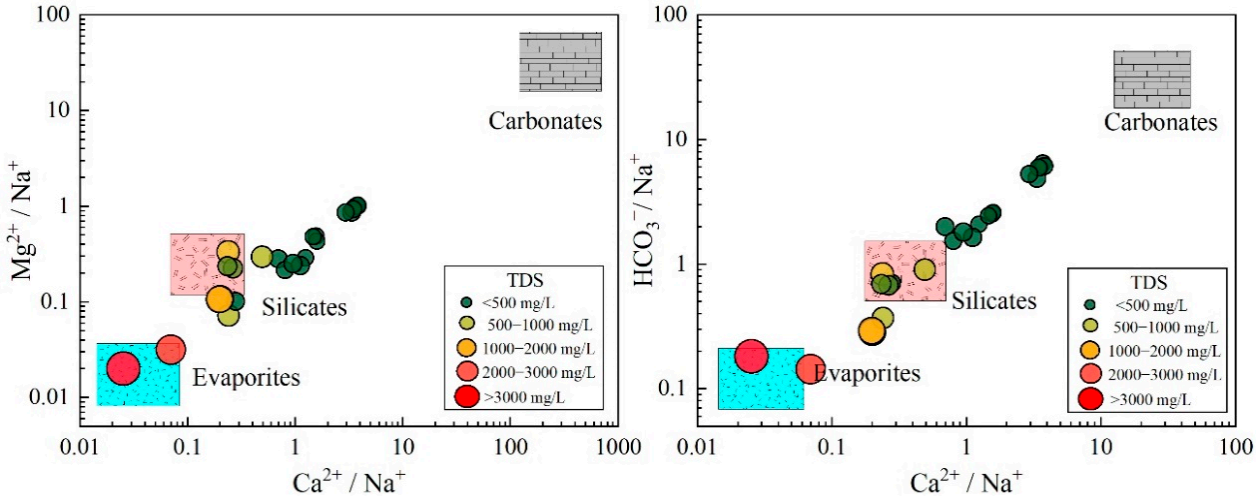


Figure 9. The endmember diagrams of (**a**) (Mg^{2+}/Na^+) versus (Ca^{2+}/Na^+) and (**b**) (HCO_3^-/Na^+) versus (Ca^{2+}/Na^+) of groundwater within the basin.

In recent years, the urbanization process has gradually accelerated, and agricultural activities are becoming increasingly intense. All of these human activities would disturb the natural hydrochemistry of groundwater in the basin. NO_3^- is an important indicator of anthropogenic inputs for groundwater chemicals. Naturally, the content of NO_3^- in natural surface and subsurface water is within 10 mg/L. Any water with NO_3^- content exceeding this geological limit is regarded as influenced by human activities. As statistically listed in Table 2, a lot of groundwater samples (79.17%) have NO_3^- content beyond 10 mg/L, indicating the disturbance of anthropogenic inputs. It can be seen from Figure 10 that most major ions presented a relatively high Spearman correlation coefficient with NO_3^- in groundwater, implying that the anthropogenic inputs of nitrogen contaminants also bring other chemicals into groundwater and result in the elevated salinity of groundwater.

To further constrain the sources of nitrogen contaminants, the relationship between (NO_3^-/Na^+) and (Cl^-/Na^+) ratios of groundwater within the basin is explored. As illustrated in Figure 11, the sampled groundwaters are plotted in the dominance among the agricultural activities and municipal sewages, indicating that both agricultural activities and municipal sewage are responsible for the elevated NO_3^- content in groundwater within the basin. However, groundwater samples with relatively high salinity (TDS) are located adjacent to the municipal sewage dominance rather than the agricultural activities dominance. This suggests that municipal sewage is responsible for the elevated salinity of groundwater in the basin rather than the agricultural activities. Although F^- is not observed with a significant positive correlation across the whole basin (Figure 10), the spatial distribution of high F^- groundwater is consistent with that of high NO_3^- groundwater in the central basin, where is the urban area of the basin. This suggests that groundwater fluoride is highly possible from municipal sewage. While the agricultural activities are not responsible for the high F^- content of groundwater in the basin.

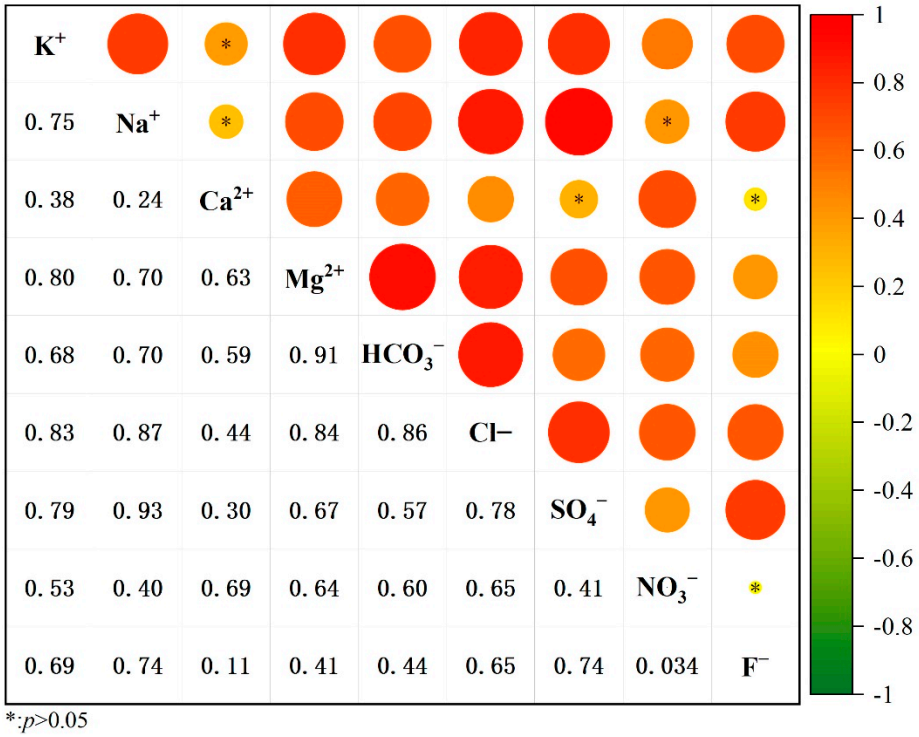


Figure 10. Spearman correlation analysis of groundwater chemical parameters.

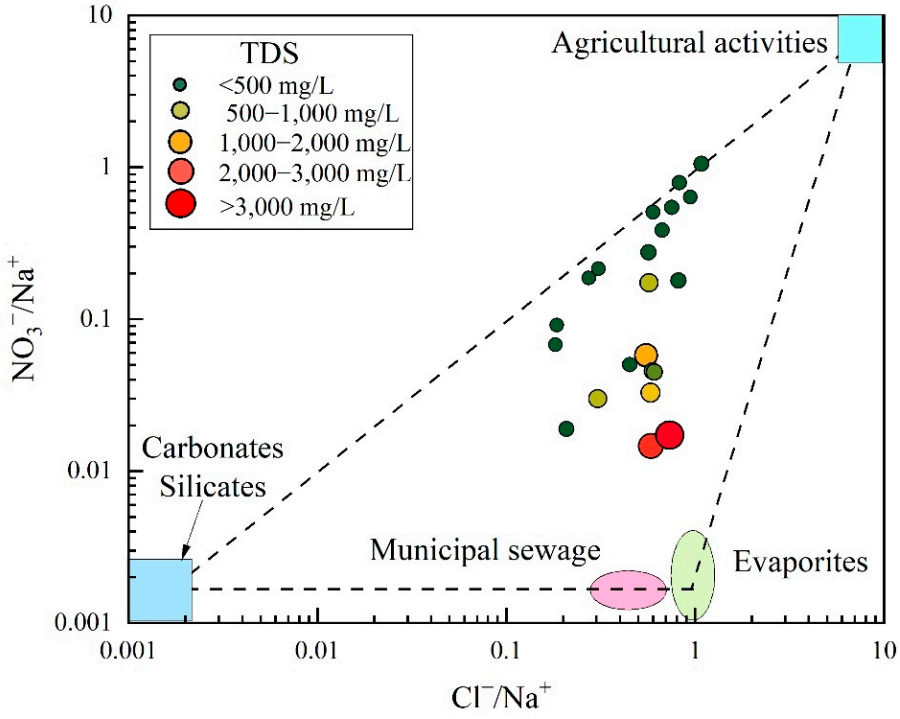


Figure 11. Relationship Diagram of (NO_3^-/Na^+) versus (Cl^-/Na^+) ratios of groundwater within the basin.

5. Conclusions

The present research focuses on the hydrochemical characteristics, quality, spatial variations, and controlling processes of groundwater in urbanized valley basins on the Tibetan Plateau. A typical urbanized valley basin named the Beichuan River basin was investigated and analyzed with integrated approaches of entropy water quality index,

human health risk assessment, irrigation quality indices, and hydrochemical analysis. The main findings are as below:

(1) Groundwater resources are slightly alkaline, with the pH in the range of 7.13 to 8.31. Groundwater presents a gradual increase of salinity from the upstream to the downstream and a relatively great variation, with the TDS ranging from 206 mg/L to 3066 mg/L. Groundwater hydrochemical facies are dominated by the HCO_3-Ca type (54.17%), followed by the Cl-Na type (33.33%), and the mixed Cl-Mg·Ca type (12.5%). Groundwater toxic substances of NO_3^-, NO_2^-, and F^- exceed the desirable limits for drinking purposes with the maximum concentration of 69.33 mg/L, 0.04 mg/L, and 3.12 mg/L, respectively.

(2) Groundwater within the basin has an EWQI value between 26.7 and 143.4. Approximately 50.00% of groundwater samples have the EWQI value less than 50 and belong to the overall water quality of Rank 1. About 33.30% and 16.70% of groundwaters have the EWQI value in the range of 50–100 and 100–150, respectively, and are categorized as the overall water quality of Rank 2 and Rank 3. Groundwater across the basin can be used for domestic usage, but that located in the lower basin should be not directly used for drinking based on the EWQI assessment.

(3) The exceedingly toxic substances would pose potential health hazards to various populations with the HI (overall non-carcinogenic health risk) value in the range of 0.592–6.255 for infants, 0.367–3.876 for children, 0.263–2.763 for adult females, and 0.339–3.411 for adult males, respectively. Only infants (29.2%), rather than the other three populations, face the high risk posed by the toxic substances across the basin. All populations are with the potential medium risk posed by the toxic substances and account for 62.5% of sampled sites for infants, 66.7% of sampled sites for children, 58.3% of sampled sites for adult females, and 66.7% of sampled sites for adult males, respectively. The health risks of groundwater for all populations are located in the downstream area.

(4) Groundwater quality for irrigation purposes has been assessed using the single indicators of EC, SAR, %Na, RSC, KR, PI, and PS. Predominant groundwater samples are suitable for long-term agricultural irrigation according to these single-indicator assessment results. Groundwater with relatively poor irrigation is dominantly located in the middle downstream area. The integrated irrigation quality assessment of the USSL, Wilcox, and Doneen diagram also demonstrated groundwater in dominated sites is suitable for long-term irrigation.

(5) Groundwater chemistry in the basin is naturally governed by water-rock interaction and evaporation. Groundwater chemical solutes are dominantly from silicate dissolution and also sporadically from evaporated dissolution. The influence of water-rock interaction on groundwater chemistry is predominantly observed in the upper reaches of the stream, while the impact of evaporation is more pronounced in the middle to lower reaches. Human activities have regulated the hydrochemical composition of groundwater in the basin. Both agricultural activities and municipal sewage are responsible for the elevated NO_3^- content in groundwater. While only municipal sewage is responsible for elevated salinity and F^- content in groundwater. Anthropogenic contaminants should be concerned to protect groundwater resources from the external negative influence of human communities in these urbanized valley basins.

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References

1. Subba Rao, N.; Das, R.; Sahoo, H.K.; Gugulothu, S. Hydrochemical characterization and water quality perspectives for groundwater management for urban development. *Groundw. Sustain. Dev.* **2024**, *24*, 101071. [CrossRef]
2. Tiwari, V.; Kumar, A.; Mukherjee, M. GIS and AHP-based groundwater recharge potential zones in urban region: A study of Ajmer City, Rajasthan, India. *Urban Clim.* **2024**, *54*, 101840. [CrossRef]
3. He, C.; Liu, Z.; Wu, J.; Pan, X.; Fang, Z.; Li, J.; Bryan, B.A. Future global urban water scarcity and potential solutions. *Nat. Commun.* **2021**, *12*, 4667. [CrossRef]
4. Garajeh, M.K.; Feizizadeh, B.; Salmani, B.; Ghasemi, M. Analyzing Urban Drinking Water System Vulnerabilities and Locating Relief Points for Urban Drinking Water Emergencies. *Water Resour. Manag.* **2024**, *38*, 2339–2358. [CrossRef]
5. Kabote, S.J. The implication of water accessibility challenges to urban water governance in Morogoro municipality, Tanzania. *Heliyon* **2024**, *10*, e28194. [CrossRef] [PubMed]
6. Yang, H.; Hou, B.; Ye, L.; Xu, S.; Xin, H.; Zhang, S. Groundwater chemical evolution characteristics and human health risk assessment in Shicheng County, Jiangxi Province. *Environ. Sci. Pollut. Res.* **2024**, *31*, 37337–37355. [CrossRef]
7. Krishan, G.; Kumar, M.; Rao, M.S.; Garg, R.; Yadav, B.K.; Kansal, M.L.; Singh, S.; Bradley, A.; Muste, M.; Sharma, L.M. Integrated approach for the investigation of groundwater quality through hydrochemistry and water quality index (WQI). *Urban Clim.* **2023**, *47*, 101383. [CrossRef]
8. 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]
9. Wang, F.; Yang, H.; Zhang, Y.; Wang, S.; Liu, K.; Qi, Z.; Chai, X.; Wang, L.; Wang, W.; Banadkooki, F.B.; et al. Solute Geochemistry and Water Quality Assessment of Groundwater in an Arid Endorheic Watershed on Tibetan Plateau. *Sustainability* **2022**, *14*, 15593. [CrossRef]
10. Zhang, M.; Wang, L.; Zhao, Q.; Wang, J.; Sun, Y. Hydrogeochemical and anthropogenic controls on quality and quantitative source-specific risks of groundwater in a resource-based area with intensive industrial and agricultural activities. *J. Clean. Prod.* **2024**, *440*, 140911. [CrossRef]
11. Naik, M.R.; Mahanty, B.; Sahoo, S.K.; Jha, V.N.; Sahoo, N.K. Assessment of groundwater geochemistry using multivariate water quality index and potential health risk in industrial belt of central Odisha, India. *Environ. Pollut.* **2022**, *303*, 119161. [CrossRef] [PubMed]
12. Vesković, J.; Deršek-Timotić, I.; Lučić, M.; Miletić, A.; Đolić, M.; Ražić, S.; Onjia, A. Entropy-weighted water quality index, hydrogeochemistry, and Monte Carlo simulation of source-specific health risks of groundwater in the Morava River plain (Serbia). *Mar. Pollut. Bull.* **2024**, *201*, 116277. [CrossRef] [PubMed]
13. Hao, Q.; Li, Y.; Xiao, Y.; Yang, H.; Zhang, Y.; Wang, L.; Liu, K.; Liu, G.; Wang, J.; Hu, W.; et al. Hydrogeochemical fingerprint, driving forces and spatial availability of groundwater in a coastal plain, Southeast China. *Urban Clim.* **2023**, *51*, 101611. [CrossRef]
14. Xiao, Y.; Hao, Q.; Zhang, Y.; Zhu, Y.; Yin, S.; Qin, L.; Li, X. Investigating sources, driving forces and potential health risks of nitrate and fluoride in groundwater of a typical alluvial fan plain. *Sci. Total Environ.* **2022**, *802*, 149909. [CrossRef]
15. Amiri, V.; Sohrabi, N.; Li, P.; Amiri, F. Groundwater Quality for Drinking and Non-Carcinogenic Risk of Nitrate in Urban and Rural Areas of Fereidan, Iran. *Expo. Health* **2023**, *15*, 807–823. [CrossRef]

16. Wani, A.M.L.; Abunada, Z.; Yenilmez, F.; Muhammetoglu, A.; Muhammetoglu, H. Comparative assessment of hydrochemical characterization and groundwater quality for irrigation in an autochthonous karst aquifer with the support of GIS: Case study of Altinova, Turkey. *Environ. Earth Sci.* **2024**, *83*, 237. [CrossRef]
17. Liu, J.; Peng, Y.; Li, C.; Gao, Z.; Chen, S. An investigation into the hydrochemistry, quality and risk to human health of groundwater in the central region of Shandong Province, North China. *J. Clean. Prod.* **2021**, *282*, 125416. [CrossRef]
18. Sinha, H.; Rai, S.C.; Kumar, S. Post-monsoon groundwater hydrogeochemical characterization and quality assessment using geospatial and multivariate analysis in Chhotanagpur Plateau, India. *Environ. Dev. Sustain.* **2024**, *26*, 20127–20157. [CrossRef]
19. 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]
20. Kim, S.H.; Kim, H.-R.; Yu, S.; Kang, H.-J.; Hyun, I.-H.; Song, Y.-C.; Kim, H.; Yun, S.-T. Shift of nitrate sources in groundwater due to intensive livestock farming on Jeju Island, South Korea: With emphasis on legacy effects on water management. *Water Res.* **2021**, *191*, 116814. [CrossRef]
21. 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]
22. Hou, Q.; Pan, Y.; Zeng, M.; Wang, S.; Shi, H.; Huang, C.; Peng, H. Assessment of groundwater hydrochemistry, water quality, and health risk in Hainan Island, China. *Sci. Rep.* **2023**, *13*, 12104. [CrossRef] [PubMed]
23. Sehlaoui, H.; Hassikou, R.; Dakak, H.; Zouahri, A.; El Hasini, S.; Iaaich, H.; Ghanimi, A.; Douaik, A. Nitrate contamination and associated health risks of the Benslimane groundwater, Morocco. *Environ. Geochem. Health* **2022**, *44*, 4343–4358. [CrossRef] [PubMed]
24. Ravindra, B.; Subba Rao, N.; Dhanamjaya Rao, E.N. Groundwater quality monitoring for assessment of pollution levels and potability using WPI and WQI methods from a part of Guntur district, Andhra Pradesh, India. *Environ. Dev. Sustain.* **2023**, *25*, 14785–14815. [CrossRef]
25. Shaw, S.K.; Sharma, A. Assessment of groundwater quality and suitability for irrigation purpose using irrigation indices, remote sensing and GIS approach. *Groundw. Sustain. Dev.* **2024**, *26*, 101297. [CrossRef]
26. Hakami, R.A.; Naser, R.S.M.; El-Bakkali, M.; Othman, M.D.M.; Yahya, M.S.; Raweh, S.; Mohammed, A.; Belghyti, D. Groundwater quality deterioration evaluation for irrigation using several indices and geographic information systems: A case study. *Desalination Water Treat.* **2024**, *320*, 100645. [CrossRef]
27. Awaleh, M.O.; Boschetti, T.; Ahmed, M.M.; Dabar, O.A.; Robleh, M.A.; Waberi, M.M.; Ibrahim, N.H.; Dirieh, E.S. Spatial distribution, geochemical processes of high-content fluoride and nitrate groundwater, and an associated probabilistic human health risk appraisal in the Republic of Djibouti. *Sci. Total Environ.* **2024**, *927*, 171968. [CrossRef]
28. Malik, A.; Yasar, A.; Tabinda, A.B.; Iftikhar, M.H.; Mukhtar, S. Health risk assessment of nitrates and fluorides ingestion and geochemical evaluation of groundwater characteristics in semi-arid regions. *Int. J. Environ. Sci. Technol.* **2024**, *21*, 8459–8486. [CrossRef]
29. Amiri, V.; Ali, S.; Sohrabi, N.; Amiri, F. Hydrogeochemical evaluation with emphasis on nitrate and fluoride in urban and rural drinking water resources in western Isfahan province, central Iran. *Environ. Sci. Pollut. Res.* **2023**, *30*, 108720–108740. [CrossRef]
30. Sarma, R.; Singh, S.K. Assessment of groundwater quality and human health risks of nitrate and fluoride contamination in a rapidly urbanizing region of India. *Environ. Sci. Pollut. Res.* **2023**, *30*, 55437–55454. [CrossRef]
31. Mukherjee, I.; Singh, U.K. Environmental fate and health exposures of the geogenic and anthropogenic contaminants in potable groundwater of Lower Ganga Basin, India. *Geosci. Front.* **2022**, *13*, 101365. [CrossRef]
32. Zendehbad, M.; Mostaghelchi, M.; Mojganfar, M.; Cepuder, P.; Loiskandl, W. Nitrate in groundwater and agricultural products: Intake and risk assessment in northeastern Iran. *Environ. Sci. Pollut. Res.* **2022**, *29*, 78603–78619. [CrossRef]
33. Flores Avilés, G.P.; Spadini, L.; Sacchi, E.; Rossier, Y.; Savarino, J.; Ramos, O.E.; Duwig, C. Hydrogeochemical and nitrate isotopic evolution of a semiarid mountainous basin aquifer of glacial-fluvial and paleolacustrine origin (Lake Titicaca, Bolivia): The effects of natural processes and anthropogenic activities. *Hydrogeol. J.* **2022**, *30*, 181–201. [CrossRef]
34. Su, H.; Li, H.; Chen, H.; Li, Z.; Zhang, S. Source identification and potential health risks of fluoride and nitrate in groundwater of a typical alluvial plain. *Sci. Total Environ.* **2023**, *904*, 166920. [CrossRef]
35. Wang, S.; Chen, J.; Zhang, S.; Bai, Y.; Zhang, X.; Jiang, W.; Yang, S. Shallow groundwater quality and health risk assessment of fluoride and arsenic in Northwestern Jiangsu Province, China. *Appl. Water Sci.* **2024**, *14*, 119. [CrossRef]
36. Alizadeh, M.; Noori, R.; Omidvar, B.; Nohegar, A.; Pistre, S. Human health risk of nitrate in groundwater of Tehran–Karaj plain, Iran. *Sci. Rep.* **2024**, *14*, 7830. [CrossRef]
37. Chorol, L.; Gupta, S.K. Hybrid analytic network process (ANP)-Entropy model, time series analysis for predicting nitrate and fluoride in groundwater and cumulative health risk assessment. *J. Clean. Prod.* **2023**, *428*, 139316. [CrossRef]
38. Araya, D.; Podgorski, J.; Kumi, M.; Mainoo, P.A.; Berg, M. Fluoride contamination of groundwater resources in Ghana: Country-wide hazard modeling and estimated population at risk. *Water Res.* **2022**, *212*, 118083. [CrossRef]
39. Davraz, A.; Batur, B. Hydrogeochemistry characteristics of groundwater and health risk assessment in Yalvaç–Gelendost basin (Turkey). *Appl. Water Sci.* **2021**, *11*, 67. [CrossRef]
40. Lu, T.; Peng, H.; Yao, F.; Nadine Ferrer, A.S.; Xiong, S.; Niu, G.; Wu, Z. Trace elements in public drinking water in Chinese cities: Insights from their health risks and mineral nutrition assessments. *J. Environ. Manag.* **2022**, *318*, 115540. [CrossRef]

41. Liu, R.-p.; Zhu, H.; Liu, F.; Dong, Y.; El-Wardany, R.M. Current situation and human health risk assessment of fluoride enrichment in groundwater in the Loess Plateau: A case study of Dali County, Shaanxi Province, China. *China Geol.* **2021**, *4*, 487–497. [CrossRef]
42. Cocca, D.; Lasagna, M.; Destefanis, E.; Bottasso, C.; De Luca, D.A. Human Health Risk Assessment of Heavy Metals and Nitrates Associated with Oral and Dermal Groundwater Exposure: The Poirino Plateau Case Study (NW Italy). *Sustainability* **2024**, *16*, 222. [CrossRef]
43. Wang, W.; Li, Z.; Su, H.; Xiao, J.; Han, F.; Li, Z. Spatial and seasonal variability, control factors and health risk of fluoride in natural water in the Loess Plateau of China. *J. Hazard. Mater.* **2022**, *434*, 128897. [CrossRef]
44. Ruan, D.; Bian, J.; Wang, Y.; Wu, J.; Gu, Z. Identification of groundwater pollution sources and health risk assessment in the Songnen Plain based on PCA-APCS-MLR and trapezoidal fuzzy number-Monte Carlo stochastic simulation model. *J. Hydrol.* **2024**, *632*, 130897. [CrossRef]
45. Schiavo, M.; Giambastiani, B.M.S.; Greggio, N.; Colombani, N.; Mastrocicco, M. Geostatistical assessment of groundwater arsenic contamination in the Padana Plain. *Sci. Total Environ.* **2024**, *931*, 172998. [CrossRef]
46. Liang, L.; Zhang, L.; Liu, C.; Zhu, J.; Wang, D. Groundwater Nitrate Contamination in Arid Areas of Haidong. *Water* **2023**, *15*, 4067. [CrossRef]
47. Wang, X.; He, K.; Dong, Z. Effects of climate change and human activities on runoff in the Beichuan River Basin in the northeastern Tibetan Plateau, China. *CATENA* **2019**, *176*, 81–93. [CrossRef]
48. Miao, X.; Lindsey, D.A.; Lai, Z.; Liu, X. Contingency table analysis of pebble lithology and roundness: A case study of Huangshui River, China and comparison to rivers in the Rocky Mountains, USA. *Sediment. Geol.* **2010**, *224*, 49–53. [CrossRef]
49. Yu, L.; Liu, S.; Wang, F.; Liu, Y.; Liu, H.; Wang, Q.; Tran, L.-S.P.; Dong, Y.; Li, W. Strategies for agricultural production management based on land, water and carbon footprints on the Qinghai-Tibet Plateau. *J. Clean. Prod.* **2022**, *362*, 132563. [CrossRef]
50. Zhang, L.; Tan, X.; Chen, H.; Liu, Y.; Cui, Z. Effects of Agriculture and Animal Husbandry on Heavy Metal Contamination in the Aquatic Environment and Human Health in Huangshui River Basin. *Water* **2022**, *14*, 549. [CrossRef]
51. WHO. *Guidelines for Drinking Water Quality*; World Health Organization: Geneva, Switzerland, 2011.
52. *GB/T 14848-2017*; Standards for Groundwater Quality. General Administration of Quality Supervision: Beijing, China, 2017.
53. Dai, X.; Liang, J.; Shi, H.; Yan, T.; He, Z.; Li, L.; Hu, H. Health risk assessment of heavy metals based on source analysis and Monte Carlo in the downstream basin of the Zishui. *Environ. Res.* **2024**, *245*, 117975. [CrossRef]
54. 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]
55. Buller, I.D.; Patel, D.M.; Weyer, P.J.; Prizment, A.; Jones, R.R.; Ward, M.H. Ingestion of Nitrate and Nitrite and Risk of Stomach and Other Digestive System Cancers in the Iowa Women's Health Study. *Int. J. Environ. Res. Public Health* **2021**, *18*, 6822. [CrossRef]
56. Adimalla, N.; Qian, H. Geospatial Distribution and Potential Noncarcinogenic Health Risk Assessment of Nitrate Contaminated Groundwater in Southern India: A Case Study. *Arch. Environ. Contam. Toxicol.* **2021**, *80*, 107–119. [CrossRef]
57. Eldaw, E.; Huang, T.; Mohamed, A.K.; Mahama, Y. Classification of groundwater suitability for irrigation purposes using a comprehensive approach based on the AHP and GIS techniques in North Kurdufan Province, Sudan. *Appl. Water Sci.* **2021**, *11*, 126. [CrossRef]
58. Hosseininia, M.; Hassanzadeh, R. Groundwater quality assessment for domestic and agricultural purposes using GIS, hydrochemical facies and water quality indices: Case study of Rafsanjan plain, Kerman province, Iran. *Appl. Water Sci.* **2023**, *13*, 84. [CrossRef]
59. Ibrahim, H.; Yaseen, Z.M.; Scholz, M.; Ali, M.; Gad, M.; Elsayed, S.; Khadr, M.; Hussein, H.; Ibrahim, H.H.; Eid, M.H.; et al. Evaluation and Prediction of Groundwater Quality for Irrigation Using an Integrated Water Quality Indices, Machine Learning Models and GIS Approaches: A Representative Case Study. *Water* **2023**, *15*, 694. [CrossRef]
60. Li, Y.; Zhang, X. Characterization of the health and irrigation risks and hydrochemical properties of groundwater: A case study of the Selian coal mine area, Ordos, Inner Mongolia. *Appl. Water Sci.* **2022**, *12*, 236. [CrossRef]
61. Yin, Z.; Lin, Q.; Xu, S. Using hydrochemical signatures to characterize the long-period evolution of groundwater information in the Dagu River Basin, China. *Front. Environ. Sci. Eng.* **2021**, *15*, 105. [CrossRef]
62. Gibbs, R.J. Mechanisms controlling world water chemistry. *Science* **1970**, *170*, 1088–1090. [CrossRef]
63. Gaillardet, J.; Dupré, B.; Louvat, P.; Allègre, C.J. Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* **1999**, *159*, 3–30. [CrossRef]

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