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Hydrochemical Characteristics and Human Health Risk Assessment of Surface Water in the Danjiang River Source Basin of the Middle Route of China's South-to-North Water Transfer Project

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Abstract: The Danjiang River basin is an important water source for the Middle Route of the South-to-North Water Diversion Project. With the shortage of water resources and the increase in pollution pressure, it is of great significance to study the hydrochemical characteristics of surface water in the Danjiang River basin and the risk to human health posed by polluted water bodies for the protection and utilization of water resources. In this paper, 40 surface water samples were collected and analyzed by innovatively adopting the sampling principle of "geological structure unit + landform unit + small watershed unit". Comprehensive mathematical statistical analysis, Piper trilinear diagrams, Gibbs diagrams, and ion ratio coefficients were used to analyze the hydrochemical composition, spatial distribution characteristics and influencing factors of surface water in the Danjiang River. The entropy weight comprehensive index method (EWQI) and the health risk assessment model recommended by the United States Environmental Protection Agency (HHRA model) were used to evaluate the water quality and potential non-carcinogenic risk of surface water in the Danjiang River source basin. The results showed that the pH of surface water in the study area was 7.02~8.77, with an average value of 8.26; and the TDS was ranged from 134 to 388 mg/L, with an average value of 252.75 mg/L. The main cations in the surface water were Ca^{2+} and Mg^{2+}, accounting for 71% and 20% of the total cations, respectively, while the main anions were HCO_3^- and SO_4^{2-}, accounting for 74% and 19% of the total anions, respectively. The hydrochemical type was HCO_3^- Ca·Mg. The hydrochemical genesis was mainly controlled by the weathering of carbonate rocks, while some ions were influenced by the weathering of silicate rocks, and human activities were also an important factor affecting the chemical characteristics of the water. The EWQI of surface water in the whole region was 8.95~25.69, and the health risk index (HI) of nitrate pollution ranged from 0.0122 to 0.2118, in which the HI ranges for children and adults were 0.0217~0.2118 and 0.0122~0.1333, respectively, indicating that the water quality of the entire study area met the Class I water standards, and the potential non-carcinogenic risk of nitrate was low. However, its impact on children was significantly higher than on adults, so it is recommended to monitor the water quality downstream of urban areas in the study area to reduce agricultural non-point source pollution and urban domestic sewage discharge and thereby reduce the potential health risks for young populations.

Keywords: hydrochemical characteristics; rock weathering; water quality evaluation; human health risk assessment; Danjiang River source

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1. Introduction

The hydrochemical composition of groundwater and river water is the result of the long-term interaction between water and the surrounding environment in the process of circulation [1–4]. The chemical composition is crucial in characterizing water environment quality, regional environmental chemical characteristics, water element distribution, and migration and transformation [5–7]. Analyzing the chemical composition and spatial variation in river water can provide vital information on the geochemical behavior of elements, rock weathering, and human activities in the basin, which is essential for the rational utilization and protection of surface water resources [8–10].

Scholars have utilized various analytical methods, including mathematical statistics, correlation analysis, simulation calculation, Piper three-line diagrams, Gibbs diagrams, ion proportional coefficient methods, and spatial variation characteristics analysis, to study the hydrochemical characteristics of major rivers worldwide and their relationship with climatic conditions and regional geological lithology [11,12]. Notable studies have been conducted on rivers such as the Amazon [13], Mackenzie [14], Lena [15], and Brahmani [16]. In China, the study of river water chemistry dates can be traced to the 1960s, when the focus was on the various types of river water chemistry in different regions of China. Since then, many scholars have studied the hydrochemical characteristics of major basins, lakes, reservoirs, wetlands, and springs in China, uncovering their formation processes and evolutionary patterns [17–23]. It has been demonstrated that chemical weathering of rocks is the primary natural control mechanism of the hydrochemical characteristics of rivers in China [24]. However, the relative contributions of various controlling factors of dissolved substances in river water, such as tectonic movement, lithology, landform, climate, hydrological characteristics, and vegetation types, vary under different climatic and lithological conditions [25]. Generally, the hydrochemical characteristics are primarily determined by the geological environmental factors of the basin. Furthermore, the study of river water hydrochemistry can provide insight into the types of rock that are weathering and the chemical weathering processes in the basin [19,26].

Excessive nitrate nitrogen in drinking water has been linked to gastric cancer and methemoglobinemia of infants in various studies [27,28]. Therefore, developing a Human Health Risk Assessment (HHRA) model based on water quality assessment is crucial to quantitatively evaluate the harm caused by nitrate nitrogen-polluted and gain a deeper understanding of its intrinsic link to human health [29]. Among the water quality evaluation models, the entropy weight comprehensive index (EWQI) is widely recognized as the most unbiased reflection of the real weight of each parameter [30]. Therefore, it is commonly employed for water quality assessment. The United States Environmental Protection Agency has released the Health Risk Assessment Model (HHRA model) for this purpose [31]. For instance, Wang et al. assessed the nitrate pollution of groundwater in Zhangjiakou City [32], Li et al. evaluated the health risk of nitrate in groundwater in the Songnen Plain [33], and Banajarani et al. [34] assessed the health risk of nitrate in aquifers in the foothills of the Western Ghats in southern India, and the corresponding water quality management recommendations and measures were proposed.

The Danjiang River, which originates in the southern foothills of the Qinling Mountains in the northwest of Shangluo City, Shaanxi Province, is the largest tributary of the Hanjiang River and a crucial water conservation area of the Middle Route of the South-to-North Water Diversion Project. Its water quantity and quality are critical to the sustainable development of the project and directly impact the water safety of Beijing, Tianjin, and Hebei. Previous studies have focused on the ecological environment, land use, and hydrology of the downstream in Danjiang River, specifically the Danjiangkou area [35–43]. However, in previous studies, the study of hydrochemical characteristics and water quality evaluation only consisted of macro-scale analysis based on the monitoring results of hydrological stations, without controlling for changes in water quality at the small watershed scale in the water source area. Moreover, the geological background and other factors were ignored in the study of the influencing factors of hydrochemical composition. At the same time, with the development of the economy and society, the pressure on the prevention and control of water resource pollution and water resource shortage in water source areas has increased. It is particularly important to obtain a comprehensive scientific understanding of the chemical composition and influencing factors of water in the area, objectively evaluate water quality, clarify water health risks and identify the sources of pollutants. Therefore, this study focuses on the surface water of the Danjiang small watershed sources. We examine the water chemistry and its influencing factors such as geology, geomorphology and hydrological process, evaluate the water quality, and quantitatively assess the risk of nitrate nitrogen pollution to human health using the HHRA model. The study aims to provide a theoretical foundation for the prevention and control of water resource pollution and risk control of drinking water health in the Danjiang source basin, thereby ensuring the safe operation of the Middle Route of the South-to-North Water Diversion Project.

2. Materials and Methods

2.1. Study Area

The study area is located in the northern region of Shangluo City, Shaanxi Province, at the source of the Danjiang River basin in the southern foothills of the Qinling Mountains. This region is an essential water source conservation area for the Middle Route Project of the South-to-North Water Diversion, with an elevation range of 699 to 1684 m and a topographical inclination towards the Danjiang River valley (Figure 1). It can be divided into three primary geomorphic units: the middle mountain area, low mountain and hilly area, and river valley and plateau area. The region comprises a well-developed river system, which is a typical mountain rainfed river system, with an average annual runoff of 482 million m^3 and an uneven distribution throughout the year. The runoff is mostly concentrated between July and October, with this period accounting for 73 to 82% of the annual total. The region experiences a continental humid climate in the southern margin of the warm temperate zone that is characterized by moderate heat and abundant rainfall. The area's average annual precipitation is 699.44 mm, and the average annual temperature is 12.8 °C (source: http://data.cma.cn/, accessed on 21 September 2022). The precipitation and temperature exhibit considerable vertical differences due to the topography. The mountainous area records an average annual rainfall of 798.8 mm and an average annual temperature of 10 to 11 °C, while the valley and plateau area records an average annual rainfall below 730 mm and an average annual temperature above 13 °C.

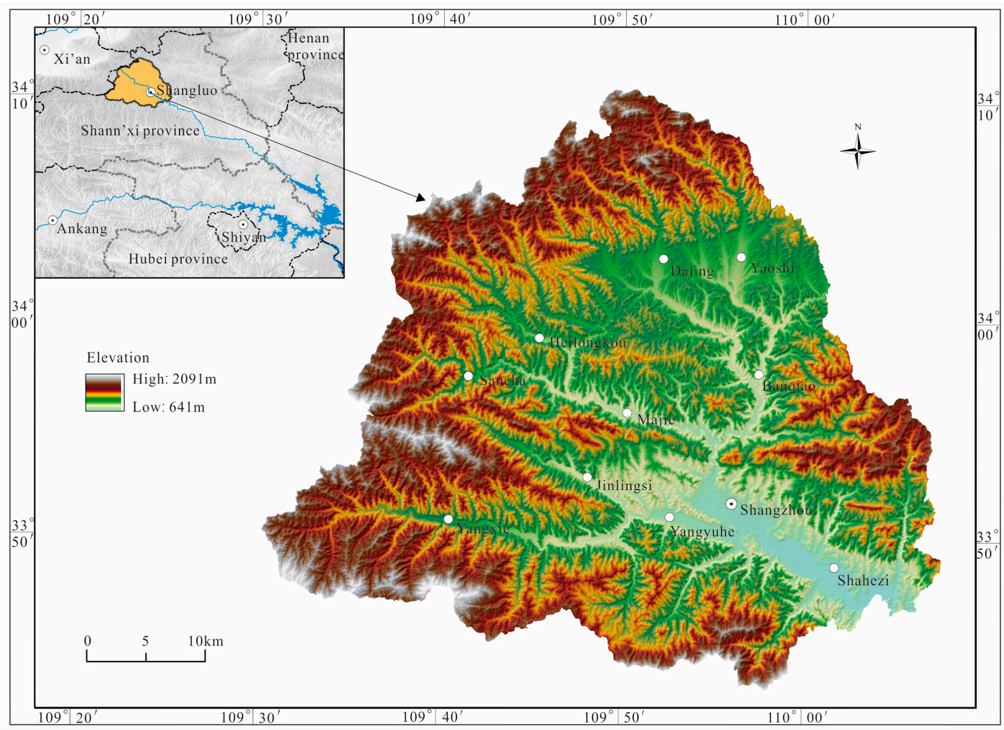

Figure 1. Location and digital elevation model (DEM) of the study area.

The study area is located at the intersection of the North China plate and the Yangtze plate and has undergone a lengthy and complex tectonic evolution [44]. As a result, the area comprises diverse rock assemblages, including Quaternary loose sediment, Cretaceous-Paleogene clastic rock, Paleozoic basic gabbro, Neoproterozoic-Triassic acid granite, Mesoproterozoic-Paleozoic basic volcanic rock, Meso-Neoproterozoic metamorphic clastic rock, Ordovician light metamorphic clastic rock, and Proterozoic-Ordovician carbonate rock (Figure 2). The resident population of the district was 472,978 in 2020. In terms of gender, the male population was 242,300 and the female population was 230,678. In terms of age distribution, the population aged 0–14 was 91,413, accounting for 19.33%, the population aged 15–59 was 290,497, accounting for 61.42%, and the population aged above 60 was 91,068, accounting for 19.25%, of whom 58,644 were aged above 65, accounting for 12.40% of the total population. The cultivated land in the area is concentrated mainly along the river valley terraces of the Danjiang River and its tributaries, with a total area of 28,742 hectares, accounting for approximately 10.76% of the total area.

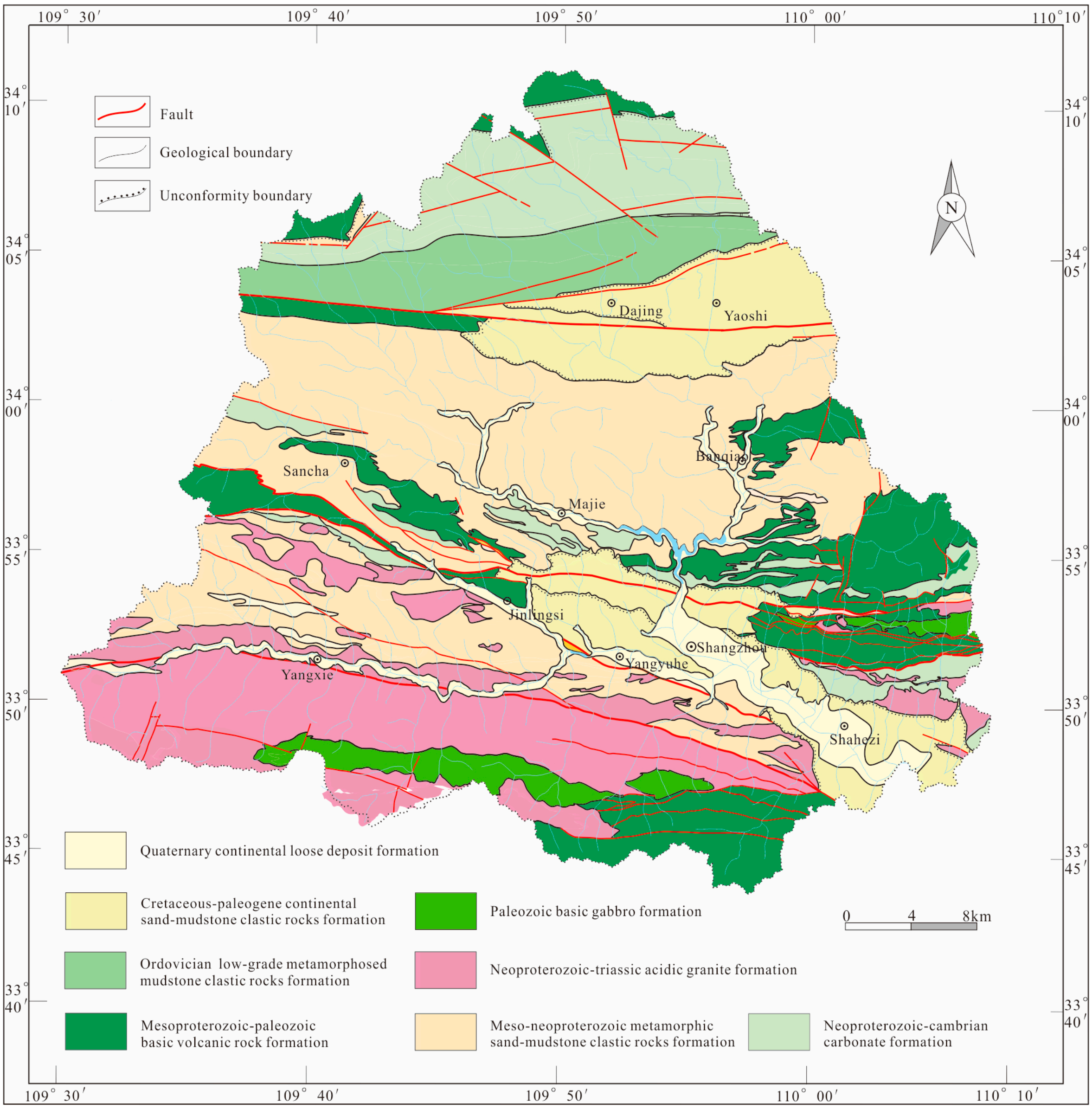

Figure 2. Map showing the geological formations and sampling sites of the Danjiang River source basin.

2.2. Sample Collection and Analysis

To comprehensively understand the hydrochemical composition, spatial variability, and water quality characteristics of the Danjiang River source basin, as well as to investigate the hydrochemical characteristics of different geological structures, landform units, and different sub-watersheds, the source region of the Danjiang river was divided into 37 small watersheds using the function of hydrological analysis module in ArcGIS. This division was based on the sampling principle of "geological structure unit + landform unit + small watershed unit". Forty surface water samples were collected in November 2021, with sampling points covering the geological structures, landform units, and small watershed units in the study area (Figure 3). After being rinsed three times with water, 5 L polyethylene plastic bottle was used to collect the samples, and the sampling depth was generally 10 cm below the water surface. At the time of sampling, the GPS location and surrounding environment of each sampling site were recorded. The on-site parameters such as pH and water temperature (T) were measured using a portable multi-parameter water quality analyzer, while Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and other cations were measured using inductively coupled plasma atomic emission spectrometry (ICP-OES). HCO_3^- was measured using hydrochloric acid titration, and Cl^-, NO_3^-, SO_4^{2-} and other anions were measured using ion chromatography (ICS-1100). Total dissolved solids (TDS) were determined using the drying method. The detection limits for K^+, Na^+, Mg^{2+}, Cl^-, and SO_4^{2-} were 0.02 mg/L, 0.01 mg/L, 0.05 mg/L, 1.0 mg/L, and 0.05 mg/L, respectively. Standard samples, parallel samples and blank samples were regularly inserted in the sample analysis, and the accuracy was checked by anion and cation balance method to ensure the absolute error was within 5%. After inspection, the test results all met the quality requirements.

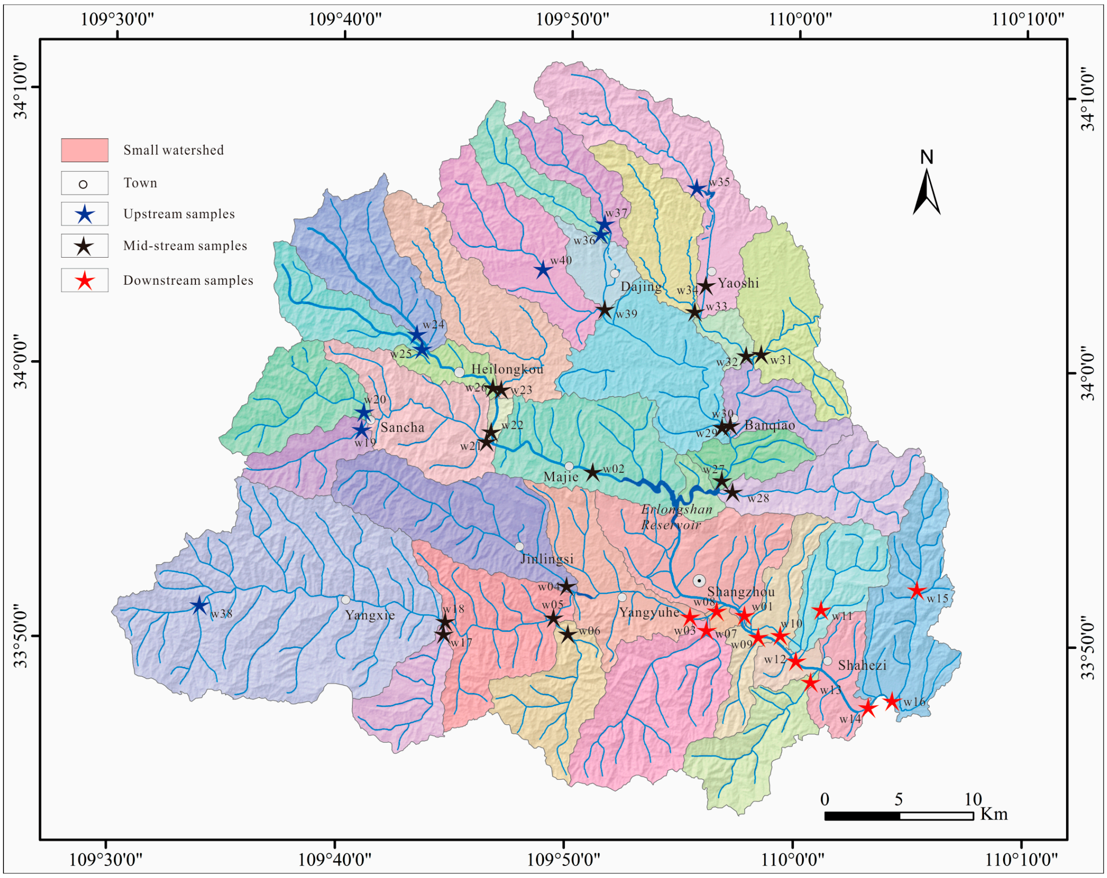

Figure 3. Map showing the drainage distribution and sampling locations in the Danjiang River source basin.

2.3. Research Methods

In the Danjiang River source zone, the hydrochemical parameters of surface water were measured and analyzed using statistical and ion correlation analysis methods in software packages such as SPSS v. 20 (IBM Corp., Armonk, NY, USA).Hydrochemical characteristics and controlling factors were examined using the Piper three-line diagram, Gibbs diagram, and ion ratio.

The entropy weight comprehensive index (EWQI) method was employed for water quality evaluation. Based on the statistical distribution characteristics of surface water chemical components and typical surface water pollution in the Danjiang River source basin, sodium, iron, manganese, sulfate, chloride, fluoride, total dissolved solids (TDS), chemical oxygen demand (COD), and nitrate nitrogen (NO_3-N) were selected as water quality analysis indicators. These indicators were used to establish an initial evaluation index matrix, determine the weight of each evaluation index, and calculate the comprehensive evaluation index (EWQI). The EWQI consolidates multiple indicators in the water quality evaluation into a single indicator that measures the overall quality of the environment. The EWQI value reflects the pollution degree of each sample. Further details on the evaluation process and water quality classification standard can be found in [45].

To quantitatively evaluate the potential health risk of nitrate nitrogen to surrounding water users through the oral intake of surface water, we used the health risk assessment model (HHRA) developed by the United States Environmental Protection Agency [31]. The population was divided into three groups based on age and gender characteristics: children (0–14 years old), adult males (>14 years old), and adult females (>14 years old). The evaluation model was:

$$HI = I_{CD}/D_{Rf} \tag{1}$$

where HI is the non-carcinogenic risk index of nitrate nitrogen (dimensionless), I_{CD} is the daily average exposure dose (mg·(kg·d)$^{-1}$), and D_{Rf} is the reference dose of nitrate nitrogen through drinking water intake, as given in Table 1. The non-carcinogenic risk threshold recommended by USEPA is 1. If $HI < 1$, the non-carcinogenic health risk is controllable; if $1 < HI < 4$, there is a moderate risk of nitrate nitrogen; and if $HI > 4$, the non-carcinogenic health risk caused by pollution is uncontrollable. Moreover, as the HI value increases, the non-carcinogenic risk increases.

According to the definition of USEPA, there are three potential contact pathways for human health risk assessment, including direct drinking water intake, air inhalation and skin absorption. The target pollutant nitrate nitrogen in water mainly enters the human body through drinking water intake, while the dose of nitrate nitrogen inhaled through skin and air contact is less than one thousandth of that absorbed by drinking water [46]. Therefore, in this study, only the potential risk of nitrate nitrogen intake through drinking water to the human body was considered. The formula for calculating the daily average exposure dose (I_{CD}) is as follows:

$$I_{CD} = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{2}$$

$$AT = ED \times 365 \tag{3}$$

In the formula, C is the concentration of nitrate nitrogen in surface water (mg/L), IR is the daily drinking water intake, EF is the exposure frequency, ED is duration, BW is the average weight of residents, and AT is the average exposure time.

Table 1. Parameters employed for human health risk assessment [47].

Parameter	Meaning	Unit	Values for Different Age Groups		
			Children	Adult Males	Adult Females
D_{Rf}	Reference dose	mg/kg·d	1.6	1.6	1.6
IR	Ingestion rate	L/d	1.8	2.79	2.20
BW	Average body weight	kg	25.9	63.8	56.5
AT	Average exposure time	d	2190	10,950	10,950
ED	Exposure duration	a	6	30	30
EF	Exposure frequency	d/a	365	365	365

3. Results and Analysis

3.1. Hydrochemical Characteristics

The statistical analysis of 40 chemicals in surface waters in the Danjiang River source basin is shown in Table 2.

Table 2. Statistics of the main surface water quality indices in the Danjiang River source zone (unit: mg/L except pH).

Reaches	Statistic	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	$SO_4{}^{2-}$	$HCO_3{}^-$	TDS	NO_3-N	Total Alkalinity
Upper reaches	Min	8.00	0.87	1.47	36.64	4.94	1.74	9.76	95.87	134.00	0.50	78.63
	Max	8.77	2.32	3.89	61.07	28.39	6.95	58.55	287.62	272.00	2.64	235.89
	Mean	8.34	1.55	2.65	51.40	16.51	3.48	40.86	183.51	215.13	1.28	152.96
	SD	0.24	0.57	0.88	7.11	8.50	2.08	21.50	71.04	40.61	0.80	58.53
Middle reaches	Min	8.07	0.95	2.06	36.64	7.41	3.48	4.88	119.84	154.00	0.95	98.29
	Max	8.49	2.91	11.40	81.43	29.63	24.33	112.21	293.62	388.00	4.18	240.81
	Mean	8.28	1.64	5.19	60.21	17.54	8.51	48.79	207.52	257.95	2.51	171.75
	SD	0.13	0.48	2.84	10.84	7.31	4.63	24.12	56.43	53.16	0.99	44.49
Lower reaches	Min	7.02	0.91	4.24	38.68	3.70	3.48	14.64	77.90	150.00	1.25	63.89
	Max	8.57	2.51	10.56	73.28	24.69	15.64	121.97	245.68	350.00	4.88	211.32
	Mean	8.17	1.68	7.96	61.85	15.67	8.69	59.67	192.21	268.31	3.28	160.66
	SD	0.39	0.45	1.94	9.57	6.92	3.40	24.24	48.71	55.93	1.20	39.69

In the study area, the pH of surface water ranged from 7.02 to 8.77, with an average value of 8.26 and a variation coefficient of 3.19%. Although pH was relatively stable within the basin, it exhibited a slight decrease in the downstream direction. The average level of total dissolved solids (TDS) was 252.75 mg/L, ranging from 134 to 388 mg/L. This level was lower than the global average of 283 mg/L reported by [48], with a coefficient of variation of 21.48%. Notably, changes in TDS were more apparent than those in pH, and they showed an increasing trend from upstream to downstream and from tributaries to the mainstream. Therefore, the water body in the study area can be classified as a low-salinity alkaline environment.

The surface water was found to have a cation equivalent concentration mean value sequence of $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. Ca^{2+} was identified as the dominant cation, with concentrations ranging from 36.64 to 81.43 mg/L and an average value of 58.98 mg/L, accounting for 65–86% of the total cation concentration, with an average value of 71%. The coefficient of variation was 17.52%, indicating a low degree of variation. Mg^{2+} was the second most abundant cation, with concentrations ranging from 3.70 to 29.63 mg/L and an average value of 16.73 mg/L. This accounted for 9–24% of the total cation concentration, with an average value of 20% and a variation coefficient of 43.55%. These findings suggest that the concentration of Ca^{2+} was more significant than that of Mg^{2+} in the basin.

Regarding anions, the average concentration order was $HCO_3{}^- > SO_4{}^{2-} > NO_3{}^- > Cl^-$, and the dominant anions were $HCO_3{}^-$ and $SO_4{}^{2-}$. The $HCO_3{}^-$ concentrations ranged from 77.90 to 293.62 mg/L with an average value of 197.74 mg/L. This represented 64% to 90% of the total anion concentration, with an average value of 74% and a variation coefficient of 28.62%. The $SO_4{}^{2-}$ concentrations ranged from 4.88 to 121.97 mg/L, with an average of 50.74 mg/L. This accounted for 6% to 26% of the total anion concentration, with an average value of 19%, and a variation coefficient 47.50%.

The Piper diagram is a valuable tool that presents the main ion composition and hydrochemical features of water related to cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-) in terms of milligram equivalent percentages [49]. Figure 4 shows that the surface water in the Danjiang River source basin had a high concentration of Ca^{2+} in the lower left corner of the cation map closer to the magnesium type area, indicating that Ca^{2+} was the primary cation followed by Mg^{2+}. Additionally, the anion diagram shows that all the water sample points were biased towards the lower left corner axis, indicating that HCO_3^- ions were the dominant anion. Based on these findings, the HCO_3^- Ca·Mg type is the main hydrochemical category for the Danjiang River source basin.

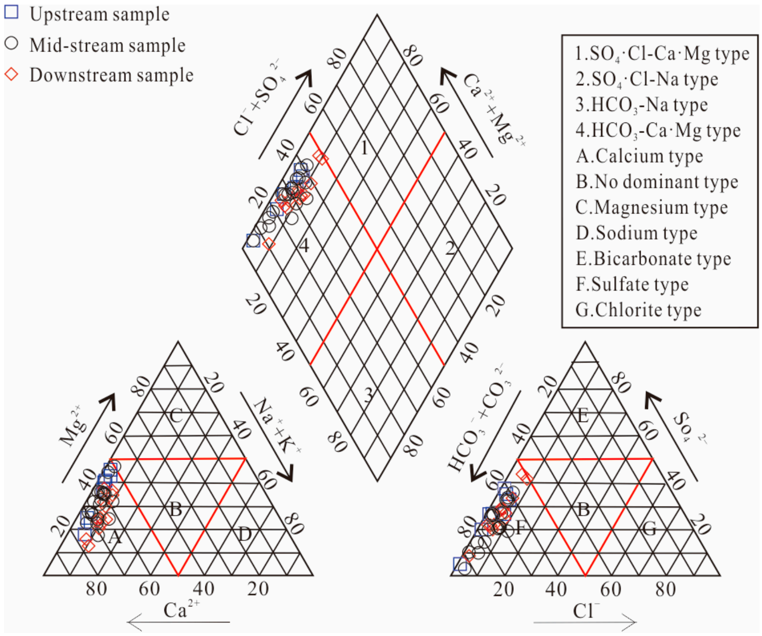

Figure 4. Piper diagram of surface water chemical composition in the Danjiang River source zone.

3.2. Spatial Variability Characteristics of Hydrochemistry

To investigate the spatial variability of hydrochemisty in the water bodies in the Danjiang River source zone, 10 surface water samples were collected and analyzed for their physicochemical properties. The samples were classified as upstream (W24 and W25), mid-stream (W26, W22, and W02), and downstream (W01, W10, W12, W14, and W16) (Figure 5). While pH and K^+ values remained relatively stable with low variation, SO_4^{2-} showed fluctuations. Moving from upstream to downstream, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3-N, and HCO_3^- showed similar variation patterns with slight upward trends, indicating higher concentrations in the downstream samples. Notably, TDS exhibited a significant uptrend, which could be attributed to surface water runoff and mixing with other sources. Moreover, the concentrations of Ca^{2+} and Mg^{2+} remained relatively stable. It can be concluded that precipitation of calcium and magnesium minerals may have occurred due to enhanced evaporation and water-rock interactions in the middle and lower reaches, considering the significant upward trend of HCO_3^-. Loose rock mineral infiltration and discharge of industrial and agricultural water alter the ion concentration in the main stream of the Danjiang River source in Shangzhou District-Shahezi Town. Cl^- and SO_4^{2-} exhibited greater variation and larger ion coefficients of variation compared with the Heilongkou-Erlongshan Reservoir section, suggesting a certain impact of point source discharge (i.e., human activities) on the surface water of the Danjiang River source basin. Industrial wastewater discharge significantly affected the Cl^-, SO_4^{2-}, and TDS concentrations at the W10 sample point.

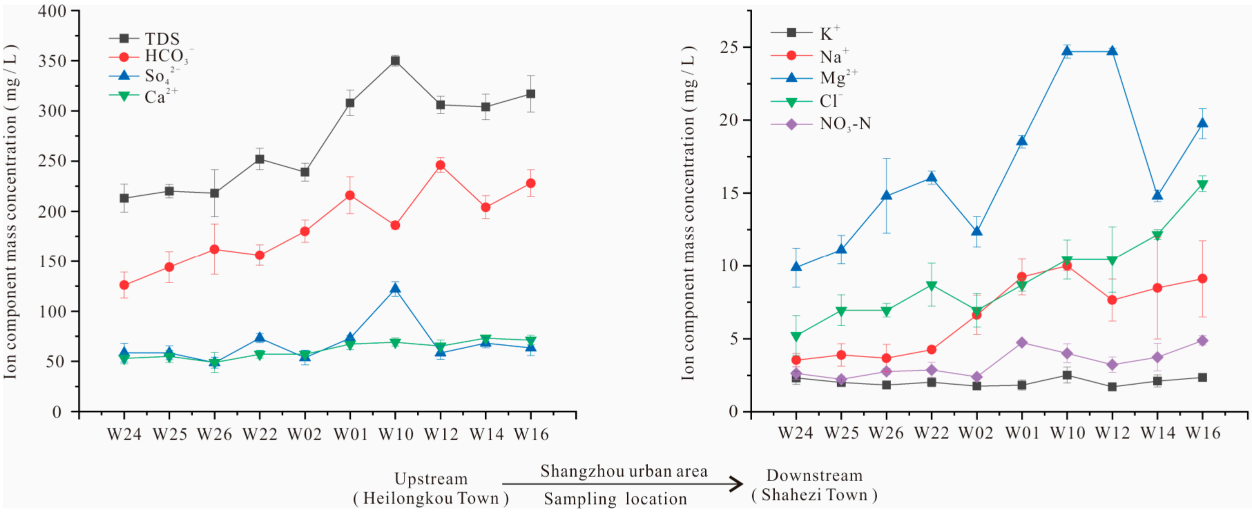

Figure 5. Spatial variations in major ion concentrations in surface water at the source of the Danjiang River.

3.3. Water Quality and Health Risk Assessment

The surface water quality of the Danjiang River source basin was classified and evaluated in this study using both the single factor index evaluation method and the entropy weight comprehensive index method. The single factor evaluation method was based on the water chemical index classification standard outlined in the 'Surface Water Environmental Quality Standard (GB3838-2002)'. The results show that all 40 samples met the Class I water standard. Similarly, using the entropy weight comprehensive index method, the calculated EWQI values of the samples ranged between 8.95 and 25.69 (Table 3), and belonged to the Class I water standard, which was consistent with the single factor evaluation method results.

Table 3. Assessment results according to computed WQI and HHRA in the Danjiang River source zone.

Sample Number	EWQI	Water Quality	Sample Number	EWQI	Water Quality	Sample Number	EWQI	Water Quality	Sample Number	EWQI	Water Quality
W01	22.68	I	W11	18.87	I	W21	16.72	I	W31	14.01	I
W02	15.72	I	W12	20.50	I	W22	17.77	I	W32	15.33	I
W03	18.12	I	W13	18.83	I	W23	16.33	I	W33	22.82	I
W04	21.99	I	W14	21.30	I	W24	15.26	I	W34	13.44	I
W05	14.33	I	W15	16.21	I	W25	15.13	I	W35	10.02	I
W06	18.51	I	W16	23.46	I	W26	16.01	I	W36	8.95	I
W07	15.74	I	W17	11.83	I	W27	17.90	I	W37	11.71	I
W08	21.92	I	W18	10.54	I	W28	14.85	I	W38	14.44	I
W09	14.63	I	W19	10.45	I	W29	15.55	I	W39	19.59	I
W10	25.69	I	W20	11.95	I	W30	20.66	I	W40	11.65	I

Furthermore, a health risk assessment was conducted using the HHRA model to evaluate the impact of nitrate nitrogen pollution in surface water. The health risk index (HI) was calculated for children as well as adult males and females based on the obtained samples. The results show that the HI for children ranged from 0.0217 to 0.2118, while for adult males and females, the HI ranged from 0.0137 to 0.1333 and 0.0122 to 0.1187, respectively (Table 4).

Table 4. Assessment results according to HHRA in the Danjiang River source basin.

Samples	Health Risk			Samples	Health Risk		
	Children	Adult Males	Adult Females		Children	Adult Males	Adult Females
W01	0.0217	0.0137	0.0122	W21	0.1061	0.0668	0.0595
W02	0.0226	0.0142	0.0127	W22	0.1065	0.067	0.0597
W03	0.0297	0.0187	0.0166	W23	0.1112	0.07	0.0623
W04	0.0401	0.0252	0.0225	W24	0.1146	0.0721	0.0642
W05	0.0411	0.0259	0.023	W25	0.1197	0.0753	0.0671
W06	0.0523	0.0329	0.0293	W26	0.1248	0.0786	0.0699
W07	0.0544	0.0342	0.0305	W27	0.1376	0.0866	0.0771
W08	0.0547	0.0344	0.0307	W28	0.1376	0.0866	0.0771
W09	0.0557	0.0351	0.0312	W29	0.1402	0.0882	0.0785
W10	0.063	0.0396	0.0353	W30	0.1525	0.0959	0.0854
W11	0.0632	0.0398	0.0354	W31	0.1541	0.097	0.0863
W12	0.0717	0.0451	0.0401	W32	0.1541	0.097	0.0863
W13	0.0755	0.0475	0.0423	W33	0.1624	0.1022	0.091
W14	0.0771	0.0485	0.0432	W34	0.1743	0.1097	0.0977
W15	0.0825	0.0519	0.0462	W35	0.18	0.1132	0.1008
W16	0.0946	0.0595	0.053	W36	0.18	0.1132	0.1008
W17	0.0967	0.0608	0.0542	W37	0.1816	0.1143	0.1018
W18	0.0984	0.0619	0.0551	W38	0.2042	0.1285	0.1144
W19	0.1042	0.0656	0.0584	W39	0.2057	0.1294	0.1153
W20	0.1046	0.0658	0.0586	W40	0.2118	0.1333	0.1187

4. Discussion

4.1. Influencing Factors of Main Ions

The use of Gibbs diagram, which relates TDS to the ratios of $(Na^+)/(Na^+ + Ca^{2+})$ and $(Cl^-)/(Cl^- + HCO_3^-)$, is a useful tool to determine the origin of ions in water and assess the effects of rock weathering, atmospheric precipitation, and evaporation-concentration on river water chemistry [50,51]. In the Danjiang River source basin, the TDS mass concentration in the surface water ranged from 134 to 388 mg/L, while the ratios of $(Na^+)/(Na^+ + Ca^{2+})$ and $(Cl^-)/(Cl^- + HCO_3^-)$ were in the ranges 0.03 to 0.16 and 0.01 to 0.09, respectively. The values for the majority of sampled locations were found in the middle and left regions of the Gibbs diagram (Figure 6), indicating that rock weathering largely influenced the hydrochemical components.

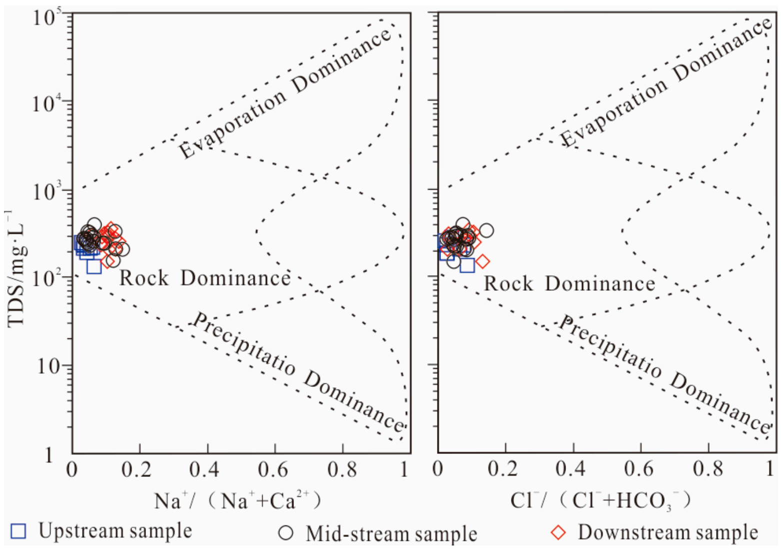

Figure 6. Gibbs diagram of surface water in the Danjiang River source zone.

The process of cation exchange adsorption plays a crucial role in shaping the composition of surface water chemistry [52]. The ratios of ($Na^+ - Cl^-$)/($Ca^{2+} + Mg^{2+}$) − ($HCO_3^- + SO_4^{2-}$) and ($K^+ + Na^+ + Cl^-$)/($HCO_3^- + SO_4^{2-}$) are used to indicate the presence of cation exchange in water [53]. In the case of ion exchange, the slope after fitting should be −1. However, the poor fitting of the aforementioned ratios in the surface water samples collected from the Danjiang River source basin suggests that the contribution of ion exchange to the surface water ions is insignificant.

4.2. Source of Main Ions

The origin of ion indices in surface water can be determined through their interdependence. Dong et al. [54] suggested that Pearson correlation analysis can provide initial insights into whether the chemical components of water have a shared source. Strong correlations among ion components indicate a common origin, while weak correlations suggest different sources. In Table 5, TDS (total dissolved solids) was found to be significantly correlated with Ca^{2+}, Mg^{2+}, HCO_3^-, and Cl^-, with correlation coefficients of 0.907, 0.733, and 0.681, respectively, suggesting that these ions predominantly contribute to TDS. Additionally, a significant correlation was observed among HCO_3^- and Ca^{2+} and Mg^{2+} ions (correlation coefficients of 0.685 and 0.851, respectively) and between Ca^{2+} and Mg^{2+}, indicating that these three ions likely originate from the weathering and dissolution of carbonate rocks. The correlation between Na^+ and K^+ was also evident, possibly derived from the dissolution of silicate rocks. In contrast, Cl^- and NO_3^- concentrations were low, which could be attributed to industrial and agricultural emissions or atmospheric precipitation. Based on the degree of correlation among ions, the sources are further discussed in groups.

Table 5. Correlation coefficients between major ions in the surface water of the Danjiang River source basin.

	pH	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**Cl^-**	**SO_4^{2-}**	**HCO_3^-**	**NO_3^-**	**TDS**
pH	1									
K^+	−0.130	1								
Na^+	−0.135	0.432 **	1							
Ca^{2+}	−0.196	0.203	0.337 *	1						
Mg^{2+}	−0.026	−0.013	−0.188	0.538 **	1					
Cl^-	−0.310	0.607 **	0.577 **	0.558 **	0.192	1				
SO_4^{2-}	−0.066	0.522 **	0.493 **	0.374 *	0.143	0.422 **	1			
HCO_3^-	−0.073	−0.188	−0.140	0.685 **	0.851 **	0.194	−0.182	1		
NO_3^-	−0.404 *	0.439 **	0.693 **	0.592 **	−0.009	0.598 **	0.488 **	0.074	1	
TDS	−0.155	0.310	0.372 *	0.907 **	0.733 **	0.598 **	0.564 **	0.681 **	0.544 **	1

Notes: ** significant correlation at the 0.01 level (two-tailed). * significant correlation at the 0.005 level (two-tailed).

4.2.1. Sources of Ca^{2+}, Mg^{2+}, and HCO_3^-

The primary control on surface water in the Danjiang River source basin is rock weathering, according to this study. According to the ratio of Ca^{2+}/Na^+ and HCO_3^-/Na^+ content in the water of 60 major rivers in the world, Gaillardet et al. [55] classified rock weathering into three types, including evaporate rock, silicate rock and carbonate rock. In the (Ca^{2+}/Na^+)/(HCO_3^-/Na^+) diagram, the surface water samples from the Danjiang River source basin fall within the silicate rock to carbonate rock area range (Figure 7a), indicating that the chemical composition of surface water in the basin is primarily controlled by carbonate rock-dominated water-rock interaction. Natural water primarily obtains Ca^{2+} and Mg^{2+} from the dissolution of carbonate rocks, silicate rocks, and evaporites, whereas HCO_3^- mainly arises from the dissolution of carbonate rocks and silicates [52,56], with minimal influence from anthropogenic activities. The ($Ca^{2+} + Mg^{2+}$)/HCO_3^- ratio should be 1:1 when carbonate rocks and silicates are the primary sources of these ions. If the ratio is less than 1, silicate rock dissolution is the primary source of these ions, whereas a ratio greater than 1 indicates that carbonate rocks are the primary source. The molar concentration ratios of $(Ca^{2+} + Mg^{2+})/HCO_3^-$ in surface water samples from the Danjiang River source basin ranged from 1.08 to 1.80 (Figure 7b), indicating that Ca^{2+}, Mg^{2+}, and HCO_3^- are primarily derived from the dissolution of carbonate rocks. The (Ca^{2+}/Na^+) and (Mg^{2+}/Na^+) ratios are often used to identify the source of major ions in water [57] and are not influenced by flow rate, dilution, or evaporation [58]. Surface water samples from the Danjiang River source basin primarily fall in the carbonate rock area (Figure 7c), supporting the conclusion that carbonate rock weathering controls the chemical composition of surface water in the Danjiang River source basin. This finding is consistent with previous analyses of the hydrochemical characteristics of the Danjiangkou Reservoir and its upstream region [35,36,41]. It is noteworthy that the upstream samples are closer to the carbonate rock weathering area, whereas the middle and downstream samples are closer to the silicate rock weathering area. This phenomenon is related to the geological formations in the study area, with the northern part comprising Proterozoic-Ordovician carbonate formations, while the central and southern surfaces are predominantly covered by (shallow metamorphic) clastic rocks, magmatic rocks, and their weathering products. This observation is consistent with the conclusion that geological formations significantly influence hydrochemical genesis in the area.

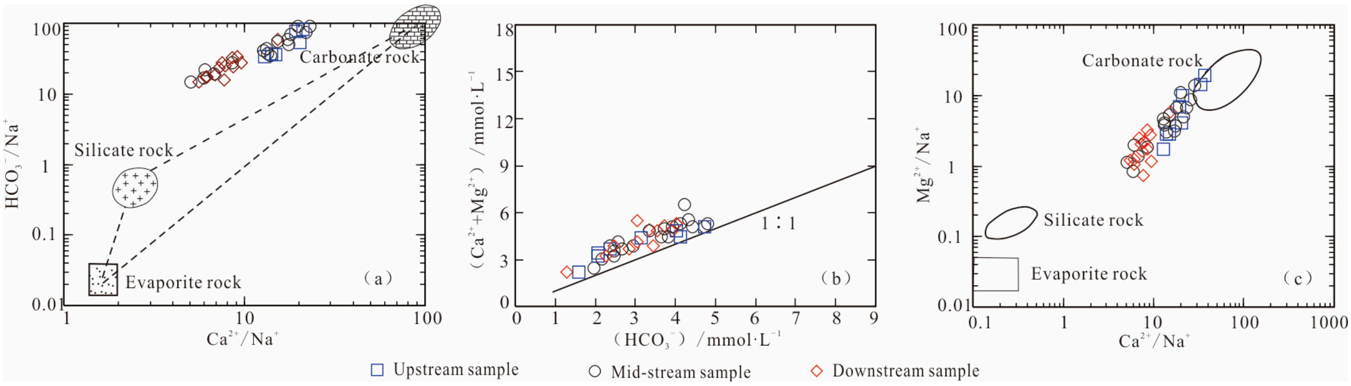

Figure 7. Relationship diagrams of (**a**) Ca^{2+}/Na^+ vs. HCO_3^-, (**b**) HCO_3^- vs. Ca^{2+}/Mg^+ and (**c**) Ca^{2+}/Na^+ vs. Mg^{2+}/Na^+ in the Danjiang River source basin.

4.2.2. Sources of Na^+, K^+, Cl^-, and NO_3^-

The study conducted by Guo et al. [59] indicated that the origin of Na^+ and K^+ in natural water is primarily attributed to the weathering products of rock salt or silicate, while Cl^- and SO_4^{2-} mostly come from evaporite dissolution. When basin evaporites control surface water cations, the $(K^+ + Na^+)/Cl^-$ equivalent ratio tends to be close to 1. However, in the Danjiang River source basin, the $(K^+ + Na^+)/Cl^-$ equivalent ratio varies between 0.59 and 3.68, with an average value of 1.56 (Figure 8a). Most samples are located above the $(K^+ + Na^+)/Cl^-$ ratio 1:1 contour line, indicating that Cl^- is insufficient to balance the presence of K^+ and Na^+. This suggests that K^+ and Na^+ may originate from the dissolution of silicate minerals such as plagioclase and potassium feldspar [60,61]. It is worth noting that sampling point 9 has a significantly higher Na^+/Cl^- value than the other sampling points, possibly due to human activities such as point source emissions from factories in the lower reaches of the Shangzhou urban area.

Cl^- is relatively stable in surface water and is almost unaffected by physical, chemical and biological processes. Its concentration only changes when water bodies with different Cl^- concentrations are mixed [62]. Therefore, the relationship between $n(NO_3^-)$, $n(NO_3^-)/n(Cl^-)$ and $n(Cl^-)$ is widely used to determine the mixing or biological process [63] of nitrate in the watershed. Specifically, higher $n(NO_3^-)/n(Cl^-)$ and low Cl^- concentrations indicate that the nitrate in the water mainly comes from agricultural activities, while lower $n(NO_3^-)/n(Cl^-)$ and high Cl^- concentrations indicate that the nitrate in the water mainly originates from domestic sewage and manure. Lower concentrations of $n(NO_3^-)$ and $n(Cl^-)$ indicate that nitrate mainly comes from soil nitrogen [64]. As shown in Figure 8b,c, the concentration of surface water samples collected from the study area of the Danjiang River source basin mainly falls within high n(NO_3^-), high n(NO_3^-)/n(Cl^-) and low n(Cl^-) categories, indicating that the NO_3^- in the region primarily comes from agricultural activities, such as the application of agricultural fertilizer, the discharge of rural domestic sewage and soil organic nitrogen. However, compared with the upstream, some sample points in the mid-stream and downstream showed a correlation trend for decreasing n(NO_3^-)/n(Cl^-) and increasing n(Cl^-), indicating that the surface water qualities in the mid-stream and downstream were affected by the mixed effects of agricultural activities and urban domestic sewage. Overall, the nitrate concentration in the surface water shows a gradually increasing trend from upstream to downstream. This is mainly due to the fact that most of the towns and farmland in the study area are distributed along rivers, and rainfall leaching, runoff erosion of riverbank soil, sewage and feces discharged by human activities all converge into the river, resulting in the gradual accumulation of nitrogen load and increasing nitrate concentration in the river. In addition, the Cretaceous Paleogene Shanyang clastic rock formation is widespread around Yaoshi Town and Shahezi Town in the study area. The degree of rock consolidation is low, and it is more prone to soil erosion under the influence of human activities, resulting in nitrogen migration to the river and accelerating nitrogen enrichment [65].

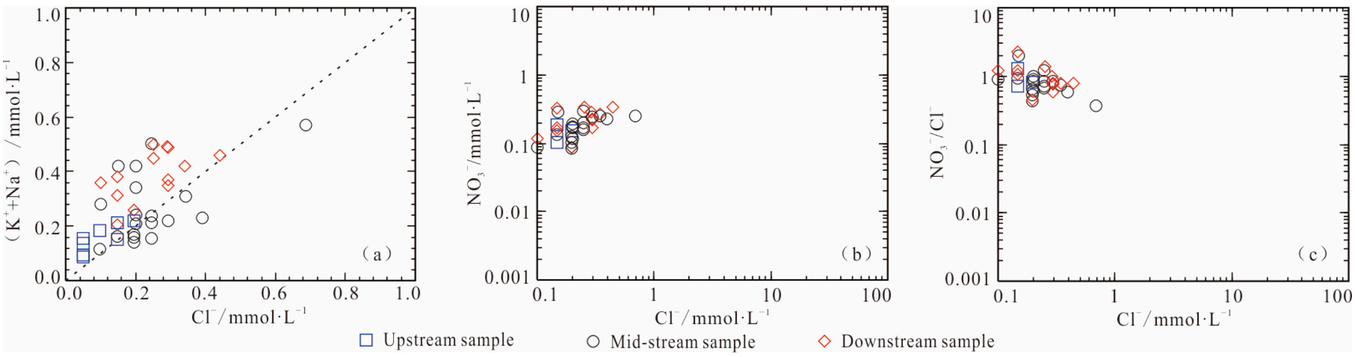

Figure 8. Relationship diagrams of (**a**) Cl^- vs. $K^+ + Na^+$,(**b**) Cl^- vs. NO_3^- and (**c**) Cl^- vs. NO_3^-/Cl^- in the Danjiang River source basin.

4.3. Water Environment Quality

4.3.1. Influence of Human Activities on Water Environmental Quality

Human activities, particularly industrial wastewater and farmland drainage, significantly influence the chemical composition and evolution of surface water, altering the contents of SO_4^{2-}, Cl^-, NO_3^-, and Na^+ ions [66]. Under natural conditions, the ratio of total hardness to alkalinity during water chemistry formation is approximately 1:1, with carbonic acid resulting from atmospheric CO_2 dissolution dominating rock weathering in the basin. However, acidic substance discharges from urban activities accelerate rock erosion, resulting in a total hardness/alkalinity ratio in water bodies greater than 1 [67]. In the Danjiang River source basin, the surface water's total hardness/alkalinity ratio ranges from 1.07 to 1.80 (Figure 9a), with an average value of 1.35, indicating the impact of acidic substances. The high values are mainly concentrated in sections with intensive human industrial and agricultural activities, such as Shangluo City, Shahezi Town, and Yaoshi Town, indicating that acidic substances emitted by human activities also have an impact on the Danjiang River's surface water in addition to natural weathering. According to He et al. [68], the undeveloped evaporite in the Danjiang river source basin and the (Ca^{2+} + Mg^{2+})/(HCO_3^- + SO_4^{2-}) ratio of surface water samples tend to be 1:1 (Figure 9b), indicating the involvement of sulfuric acid in carbonate dissolution. Moreover, the average (Ca^{2+} + Mg^{2+})/HCO_3^- and SO_4^{2-}/HCO_3^- equivalent ratios of the samples were 1.37 and 0.36, respectively, indicating that both sulfuric acid and carbonic acid are involved in the chemical weathering process of carbonate rock salt in the basin (Figure 9c). Sulfuric acid is primarily derived from sulfur oxides produced from human activities, and diffuses into the atmosphere and dissolves in water [67].

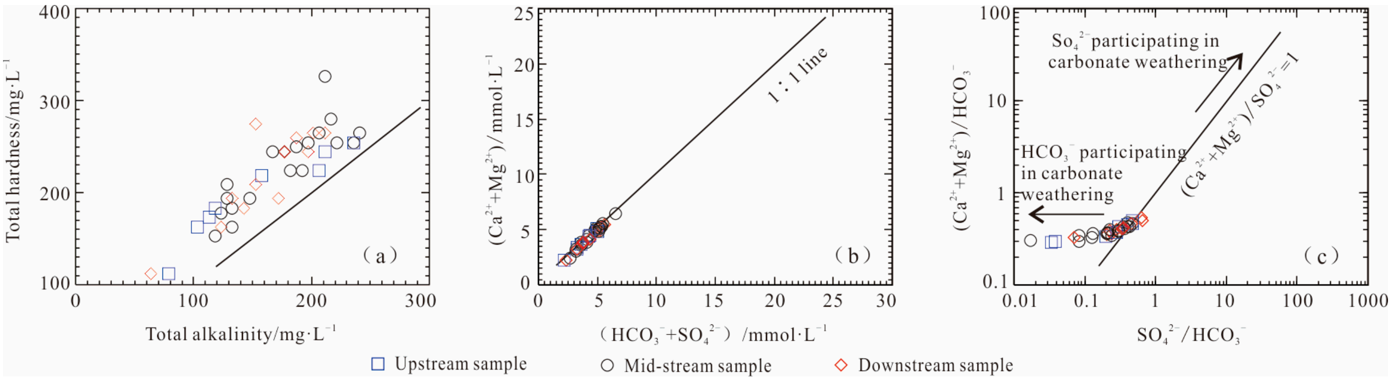

Figure 9. Relationship diagrams of (**a**) total hardness vs. Alkalinity, (**b**) Ca^{2+} + Mg^{2+} vs. HCO_3^- + SO_4^{2-} and (**c**) (Ca^{2+} + Mg^{2+})/HCO_3^- vs. SO_4^{2-}/HCO_3^- in the Danjiang River source zone.

Numerous previous studies have investigated the water quality of the Danjiang River source basin. For instance, Wang et al. [69] conducted a study on the water quality of 14 sections of the Hanjiang River and the main branch of the Danjiang River in Shaanxi Province from 2008 to 2012. They found that the water quality of the Danjiang section was primarily Class II and Class III, with notable spatial differences and regional distribution characteristics of comprehensive pollution. Pollution was more significant in the urban areas than in the suburbs, and the downstream pollution was higher than the upstream pollution in each administrative section. In another study, Zhang Jin [70] used the fuzzy comprehensive index method to comprehensively evaluate the water quality of the Majie, Zhangcun, Danfeng, and Yueri sections in Shangluo City in the upper reaches of the Danjiang River from 2018 to 2021. The study concluded that the water quality of the Yueri section was lower than that of the Majie section in the upper reaches.

This study used the entropy weight comprehensive index evaluation method to assess the water quality of 40 surface water samples in the Danjiang River basin. The obtained EWQI values ranged from 8.95 to 25.69, indicating that the water in the study area met the Class I water quality standard and was of excellent quality. This was attributed to the implementation of robust water resource protection measures by the local government in recent years. When sorting the EWQI values of the water quality samples, it was observed that the samples with EWQI values above 20 were mainly distributed in Shangzhou City and Shahezi Town along the main stream of the Danjiang River. These areas had dense residential populations, significant discharge of industrial and domestic wastewater, and slightly higher EWQI values than the tributaries in mountainous areas with less impact from human activities. Therefore, to safeguard water quality, water quality protection and monitoring efforts should be enhanced in areas with higher levels of human economic and social activities.

4.3.2. Health Risk Assessment

In this study, nitrate nitrogen was included in the human health risk assessment. The risk index calculation model showed that the health risk index (HI) due to nitrate nitrogen in surface water consumed as drinking water in the Danjiang River source area ranged from 0.0217 to 0.2118 for children, from 0.0137 to 0.1333 for adult males, and from 0.0122 to 0.1187 for adult females. It is thus clear that the risk of nitrate pollution in surface water in the Danjiang River source basin was at a relatively low level, and was significantly lower than the acceptable risk level for non-carcinogenic chronic toxic effects, indicating minimal risk to human health. However, the study found that children were more vulnerable to polluted water sources than adults, with a significantly higher health risk index scores, indicating that the younger population are more sensitive with relatively weak resistance to polluted water, which warrants further attention. The limit concentration of nitrate nitrogen in drinking water stipulated by the World Health Organization (WHO) and China is 10 mg/L, and the concentration of nitrate nitrogen in the study area ranged from 0.52 to 4.88 mg/L, with an average value of 2.56 mg/L, which was lower than the WHO limit. However, the value of nitrate nitrogen showed an increasing trend in downstream urban areas, and the human health risk index of nitrate nitrogen was also higher than that in the upstream areas. According to the statistics of the Shangzhou Center for Disease Control and Prevention in 2020, there are 36 cases of goiter patients in the district, mainly distributed in urban areas. As mentioned earlier, this may be related to the unreasonable discharge of agricultural waste and urban sewage. After the nitrate in enters the mouth, it is converted into nitrite by the nitrate reducing bacteria in saliva, which increases the risk of diseases such as methemoglobinemia, diabetes, spontaneous abortion, thyroid disease and gastric cancer [71]. Therefore, it is recommended to focus on protecting and monitoring the water quality in the downstream area and to pay more attention to the health risks of younger age groups with poor resistance.

4.4. Uncertainty Analysis

Water environmental health risk assessment mainly includes the harm to human health caused by toxic pollutants directly ingested through contact routes such as food in the water, drinking water, and breathing. In this paper, the evaluation of the human health risk is only focused on the impact of drinking water intake, without considering other toxic substances and exposure routes. Thus, the actual health risk level of water nitrate pollution may be greater than the risk value reported in this study. In addition, the health risk assessment of nitrate pollution lacks data for the wet season and long periods with surface water, and the model parameters used are mainly determined based on previous research results in Shaanxi Province. However, in fact, there are differences in human characteristics and lifestyles among southern, northern and central Shaanxi regions, so there may be some errors in the evaluation parameters of health risks. Therefore, the research results of this paper are preliminary and need to be further improved in future work to provide better support for scientific management and decision-making related to water resources protection and utilization.

5. Conclusions

1. The surface water in the Danjiang River source basin is characterized by a low mineralization and slightly alkaline environment. The average concentration of cation equivalents is in the order of Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}, with Ca^{2+} and Mg^{2+} being the dominant cations. The average concentration of anions is in the order of HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-, with HCO_3^- and SO_4^{2-} being the dominant anions. The hydrochemisty of the water is characterized as HCO_3^- Ca·Mg type.
2. Our comprehensive study based on Gibbs diagrams, ion ratio coefficients, and factor analysis shows that the solutes in the water of the Danjiang River are mainly controlled by rock weathering, while agricultural activities and urban domestic sewage discharge also have certain impacts on the chemical components of the river water.
3. The results of the single-factor evaluation method and the entropy weight comprehensive index method show that the surface water quality in the Danjiang River source basin meets the Class I water quality standards. Overall, the water quality characteristics of the tributaries are better than the mainstream sections, and the upstream sections are better than those of the downstream areas. Additionally, the non-carcinogenic potential risks of nitrate nitrogen were low and within controllable ranges, but the impact on children was significantly higher than that on adults. Therefore, it is recommended to strengthen water quality management downstream of urban areas within the region, rationally plan the structure of industrial and agricultural production, and reduce the concentration of nitrate nitrogen in water bodies to mitigate health risks for vulnerable young populations with weaker resistance.

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Conflicts of Interest: The authors declare no conflict of interest.

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