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Hydrogeochemistry and Isotope Hydrology of Surface Water and Groundwater in the Mountain Watersheds of Daqing River, North China

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Abstract: Surface water and groundwater interaction variations in time and space are crucial for effective water management, especially in low-precipitation regions. To comprehensively determine the hydrochemical characteristics and interaction processes of surface water and groundwater and to investigate the decreasing causes of water resources in semi-arid mountainous watersheds under changing environments, intensive field surveys were conducted in the Daqing River watershed, a tributary of the Haihe River basin in northern China, during two different times of the year: after the rainy season (September 2018) and before the rainy season (July 2019). Sixty surface water and groundwater samples were collected along the mountainous watershed. Using a combination method of hydrogen and oxygen stable isotope tracing and hydrochemical analysis, the hydrogen and oxygen isotopes and hydrochemical characteristics of surface water and groundwater in the mountainous watershed of the Daqing River were analyzed. Furthermore, the effect of elevation (altitude) on isotopes was discussed, and the correlation between hydrogen and oxygen isotope composition and hydrochemical characteristics was obtained. The results were processed using endmember mixing analysis to determine the amount of contribution of the surface water and groundwater interaction processes. The results show that the hydrochemical characteristics are relatively stable in the mountainous watersheds of the Daqing River, and the surface water and groundwater are mainly of the HCO_3-Ca type. The slope of the local meteoric water line is smaller than the slope of the global meteoric water line, and the δD and $\delta^{18}O$ in surface water and groundwater show a good linear relationship both before and after the rainy season. There is a decreasing trend of the value of $\delta^{18}O$ in surface water samples with decreasing altitude, but a decreasing trend of the value of $\delta^{18}O$ in groundwater samples is not obvious. The evaporation intensity of surface water is stronger after the rainy season than before the rainy season, and the connection between the surface water and the groundwater is stronger before the rainy season. Influenced by topographic conditions and other factors, the exchange of surface water and groundwater is frequent, and there is a large difference in the exchange ratio before and after the rainy season. The exchange ratio can be more than 50% after the rainy season. Thus, the reasons for decreasing water resources in the mountains can be implied to be due to the increasing hydraulic gradient between the mountains and the piedmont plains, and the water resources are discharged more in the form of groundwater to the downstream. The conclusions help to enhance the understanding of the water cycle in the mountainous watershed and can provide some theoretical basis for the sustainable development and utilization of water resources in the Haihe River basin and the regional water ecology of the Xiong'an New Area.

Keywords: Haihe River; Daqing River; mountain watershed; isotopes; hydrochemistry; meteoric water line

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1. Introduction

Mountain rivers are important pathways connecting upland and lowland environments, regulating the supply, transport, and storage of organic and inorganic substances [1,2]. There are lots of mountains in China, accounting for 69% of the country's land area. Rivers originating from the mountains provide more than half of the freshwater resources and nourish the socio-economic system of the downstream plains. Surface water and groundwater in nature are not isolated hydrological systems but interact with each other under various topographic and climatic backgrounds, which directly affect the quantity and quality of surface water and groundwater [3,4]. Detailed information on water quality is a crucial issue for the sustainable management of water resources [5–7]. Groundwater resources play a vital role in semi-arid regions and have become critical for the drinking and economic sectors [8,9]. The transformation of rivers and groundwater is an important part of the water cycle in the basin and is fundamental to research on river maintenance mechanisms and renewable groundwater capacity [10,11]. Therefore, the interaction between surface water and groundwater is the core and hotspot of water cycle and water resources research [12].

In the study of the interaction between groundwater and surface water, the use of environmental tracers to explore the formation causes, storage conditions, migration and transformation mechanisms of water is one of the effective means to identify and quantify the interaction between surface water and groundwater [13]. Variations in isotope concentrations in different water can trace their formation and transport patterns [14,15]. It can explore the origin, age and recharge relationship of groundwater with surrounding water by tracing the isotopic information retained in water related to the environmental evolution processes in its source sites. Ramita et al. [16] studied the interconnection between surface water and groundwater in the Hanumant River basin in the Kathmandu Valley of Nepal with a hydrochemistry and stable isotopes approach. Sarah et al. [17] revealed the contribution of rainfall and shallow groundwater to runoff and the interaction between surface water and groundwater in the Middleburg region of South Africa through isotopes. Hao et al. [18] studied the composition characteristics of stable isotopes and the distribution of surface water and groundwater in the Lake Ebey basin in arid regions and discussed the recharge relationships between different water bodies.

The Haihe River basin is located in the semi-arid and semi-humid climate zone of China. Influenced by natural and anthropogenic factors, water resources and water environment problems are becoming increasingly serious and have become a hot spot for sustainable development research in China [19]. In recent years, the proportion of water resources formed by precipitation in the Haihe River basin has been lower than in normal years, and the water resources situation is more tense when the decrease in the amount of groundwater resources is higher [20]. The interaction between surface water and groundwater in the Haihe River basin is complex, and the current studies that are mainly on the groundwater and its water sources have been investigated in combination with isotope techniques in the Baiyangdian Lake area [21–24]. In contrast, the quantitative analysis of surface water and groundwater transformations in source flow areas is still in the exploration stage [25]. The Daqing River is an important tributary of the Haihe River. It is in the upper stream of the Xiong'an New Area and is responsible for the water supply security and ecological security of the Xiong'an New Area. It is well known that the establishment of the Xiong'an New Area is a major historical strategic choice, which is a part of the millennium plan and a national event in China. The degree of water resource development and utilization in the Daqing River basin is high, and problems such as decreasing surface water and the over-exploitation of groundwater are prominent [26], which not only affect social and economic development but also lead to serious ecological and environmental problems and bring great challenges to the sustainable development of the basin.

Therefore, the mountain watersheds of the Daqing River basin were selected as the research object in this study. Combining field investigation and indoor analysis, this study analyzes the hydrogen and oxygen isotopes and hydrochemical characteristics of surface water and groundwater in the basin using environmental isotope and hydrochemical techniques. This study also discusses the effect of altitude on hydrogen and oxygen isotopes and studies the interaction between surface water and groundwater in the mountainous watershed of the Daqing River. This is of great significance for enhancing the understanding of the water cycle in mountain basins and understanding the interaction and transformation relationship between surface water and groundwater for the rational utilization and effective protection of water resources in mountainous areas, as well as preventing and controlling water pollution. This study also provides a theoretical basis for the study of the water cycle in the basin under changing environments, the research on water resources and the water environment in the Haihe River basin, and the regional water resources management in the Xiong'an New Area.

2. Study Area

The Haihe River is the largest water system in North China and is one of the seven major rivers in China. The Daqing River basin is a major tributary of the Haihe River, originating from the eastern Taihang Mountains, located at 113°34′3″–117°46′7″ E, 38°4′42″–40°3′2″ N. The basin area is 43,060 km^2, with a river length of 275 km, an average width of 156 km, and an average slope of 5.22%, and the average annual runoff is 4.3×10^8 m^3. The Daqing River basin has a warm temperate monsoon climate with four distinct seasons and uneven precipitation distribution throughout the year, mainly concentrated from July to September. The average annual rainfall is between 500 and 700 mm, and heavy rain often occurs in July and August. The surface-exposed lithology is granite gneiss, limestone and quaternary loose accumulation. The terrain is dominated by mountains and basins. The soil of the mountains is mainly coarse bone soil, and the hills and platforms around the basin are covered with loess (SL665-2014). Most of the rivers in the basin belong to typical pre-mountain belt rivers, and their flow direction is from northwest to southeast. Through the continuous scouring, dissolution and physical weathering of surface water, the region has gradually evolved into a complex karst landscape [21]. The bedrock in the study area is dominated by carbonates of the Jixian system in the Sinian Suberathem, with high silica-magnesium content. Under the action of internal and external geological stresses, the dissolution phenomenon is uneven and is subject to atmospheric rainfall recharge [27,28].

According to the water resource zoning map of the Haihe River basin provided by the Haihe River Conservancy Commission (HRCC), the Daqing River basin is mainly composed of two geomorphic units: the upper mountainous area in the west and the middle and lower reaches of the plain area in the east, accounting for 43% of the basin area [29]. The basin is fan-shaped and divided into two branches, north and south. The south branch is mainly composed of 6 tributaries: the Ci River (CH), Sha River (SH), Tang River (TH), Jie River (JH), Cao River (CH2) and Bao River (BH). After entering the plain, the Ci River merges with the Sha River and flows into the Zhulong River. The North Branch is mainly composed of four tributaries: the Zhongyi River (ZY), Beiyi River (BY), Juma River (JM) and Dashi River (DS). After entering the plain, the Juma River is divided into the North Juma River and the South Juma River. These ten tributaries flow into the Baiyangdian Lake. The terrain of the basin is high in the northwest and low in the southeast, with a height difference of nearly 2800 m (Figure 1).

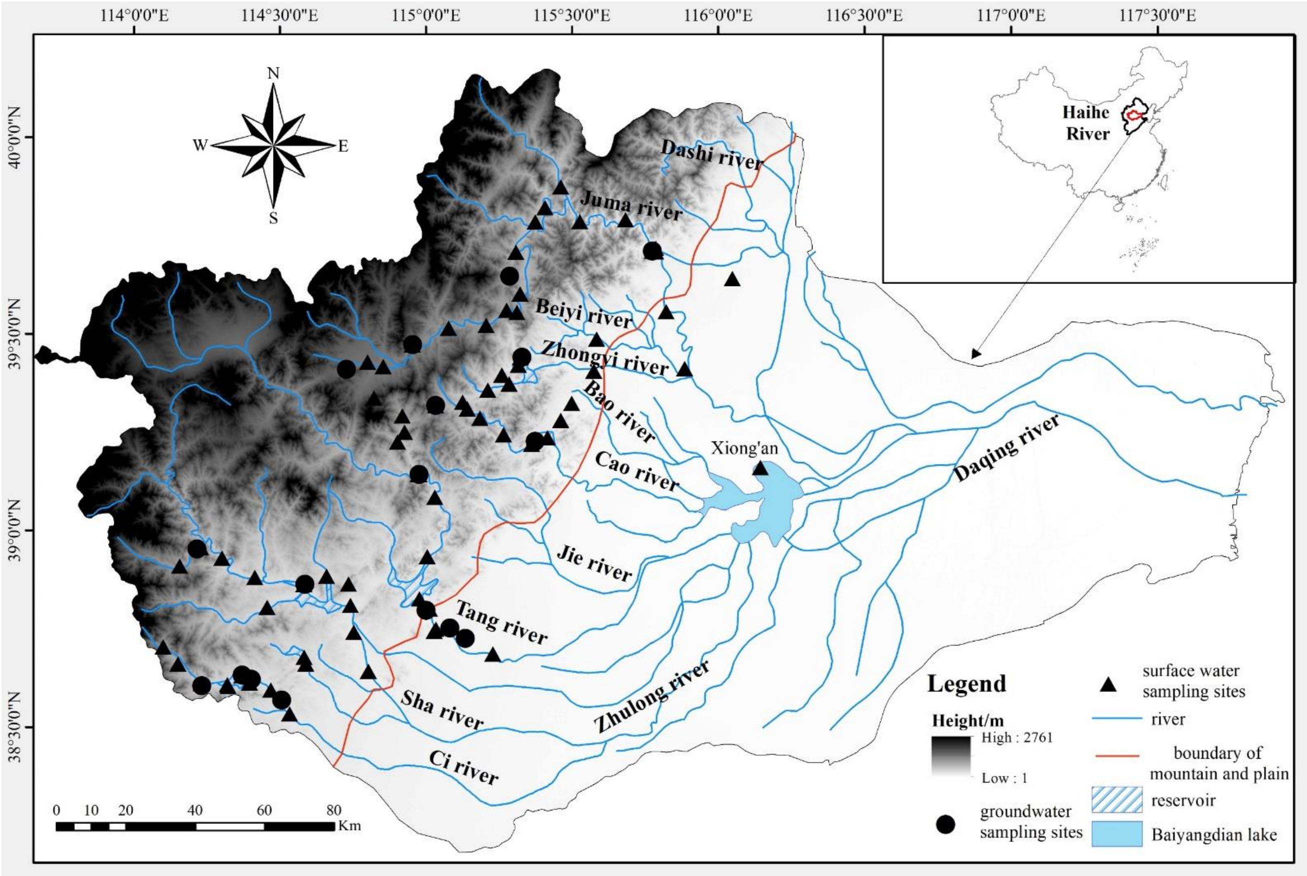

Figure 1. Distribution of water sample collection locations in the mountainous watershed of Daqing River.

3. Methodology

3.1. Sampling

There are only six tributaries of surface runoff in the mountainous area of the river basin, including the CH, SH, TH, CH2, ZY and JM rivers, with a total of sixty samples, including forty-three surface water samples and seventeen groundwater samples and three rainwater samples. Two samplings sessions were completed in September 2018 (after the rainy season) and July 2019 (before the rainy season) in 100 mL small-mouth polyethylene bottles, and the locations of the sampling sites were located and recorded with GPS (Figure 1). All water samples were stored in a refrigerator at 4 °C for analysis of the eight ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, $HCO_3{}^-$) and hydroxide isotopes (δD, $\delta^{18}O$) in the analyzed water samples, and all samples were analyzed and tested in the laboratory of the Center for Agricultural Resources Research, Chinese Academy of Sciences.

3.2. Laboratory Work

Hydrogen and oxygen stable isotope compositions in surface water, groundwater and rainwater samples were determined by an isotope mass spectrometer (L2120-I Isotopic H_2O; Picarro-i2120, Santa Clara, CA, USA). The values of stable isotopes $^2H/^1H$ or $^{18}O/^{16}O$ in natural water are very small. The results of hydrogen and oxygen stable isotope determinations are expressed as the thousandths of a percent deviation (in ‰) relative to the Vienna Standard Seawater (VSMOW), that is, the standard deviation of the isotope ratio in the sample (R · $^2H/^1H$ or $^{18}O/^{16}O$) relative to the corresponding ratio in VSMOW, calculated by Clark and Fritz [30] and Kendall and Mcdonnell [31] as,

$$\delta = \frac{R_{sample} - R_{VSMOW}}{R_{VSMOW}} \times 1000‰ \quad (1)$$

where R_{sample} and R_{VSMOW} represent the ratios of isotopes ($^{18}O/^{16}O$, $^2H/^1H$) in the samples and standards, respectively, and the precision of Picarro-i2120 is ±0.5‰ for δ^2H and ±0.2‰ for $\delta^{18}O$.

All water samples were filtered through a 0.22 µm filter membrane before measurement, and then diluted at a certain dilution level and analyzed for the concentration of major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, $HCO_3{}^-$) by ion chromatography (ICS-2100, Dionex, Sunnyvale, CA, USA). $HCO_3{}^-$ and $CO_3{}^{2-}$ in water were titrated by double indicator titration, and the anion and cation equilibrium of the analyzed samples was verified to ensure a plausible error within ±5%.

3.3. Transformation Relationship between Surface Water and Groundwater

Stable hydrogen and oxygen isotope methods can identify the source of runoff, the division of river runoff, and the conversion of surface water and groundwater [11,32]. The principle of division is based on the hydrochemical and isotopic mass balance method to estimate the conversion between surface water and groundwater. The formula is as follows:

$$f = (Q_g/Q_s) \times 100\% = (C_s - C_b)/(C_g - C_b) \times 100\% \quad (2)$$

where Q_s is the flow of water source I; Q_g is the flow of water source II; C_s is the $\delta^{18}O$ value of water source I; C_b is the $\delta^{18}O$ value of the upstream water; and C_g is the $\delta^{18}O$ value of water source II.

In addition, the measured data such as isotopes and hydrochemical characteristics were statistically analyzed using Microsoft Office Excel, Origin software and Statistical Product and Service Solutions (SPSS) to elaborate on the spatial and temporal distribution characteristics and variability among different water bodies.

4. Results and Analysis

4.1. Analysis of Hydrochemical Characteristics

Figure 2a–d shows the average concentrations of anions and cations in the surface water and groundwater of six rivers, including the CH, SH, TH, CH2, ZY and JM rivers, which were sampled twice in July and September. Both sampling results showed that the main cations in those six rivers were Ca^{2+} and Mg^{2+}, with concentrations of 2.05–2.82 mEq/L and 0.56–3.95 mEq/L, respectively, while the concentrations of the remaining cations were very low. Anions were dominated by $HCO_3{}^-$ and $SO_4{}^{2-}$, with concentrations of 1.17–5.95 mEq/L and 0.15–2.41 mEq/L, respectively, while the remaining anion concentrations, except for individual watersheds, were basically 1 mEq/L and below. Specifically, the $HCO_3{}^-$ concentration in the surface water of the ZY and JM rivers in September was significantly lower than in July. The main reason is that July and August are the rainy season, with high rainfall and recharge, and the large amount of incoming water plays a certain dilution role in the ion concentration of surface water.

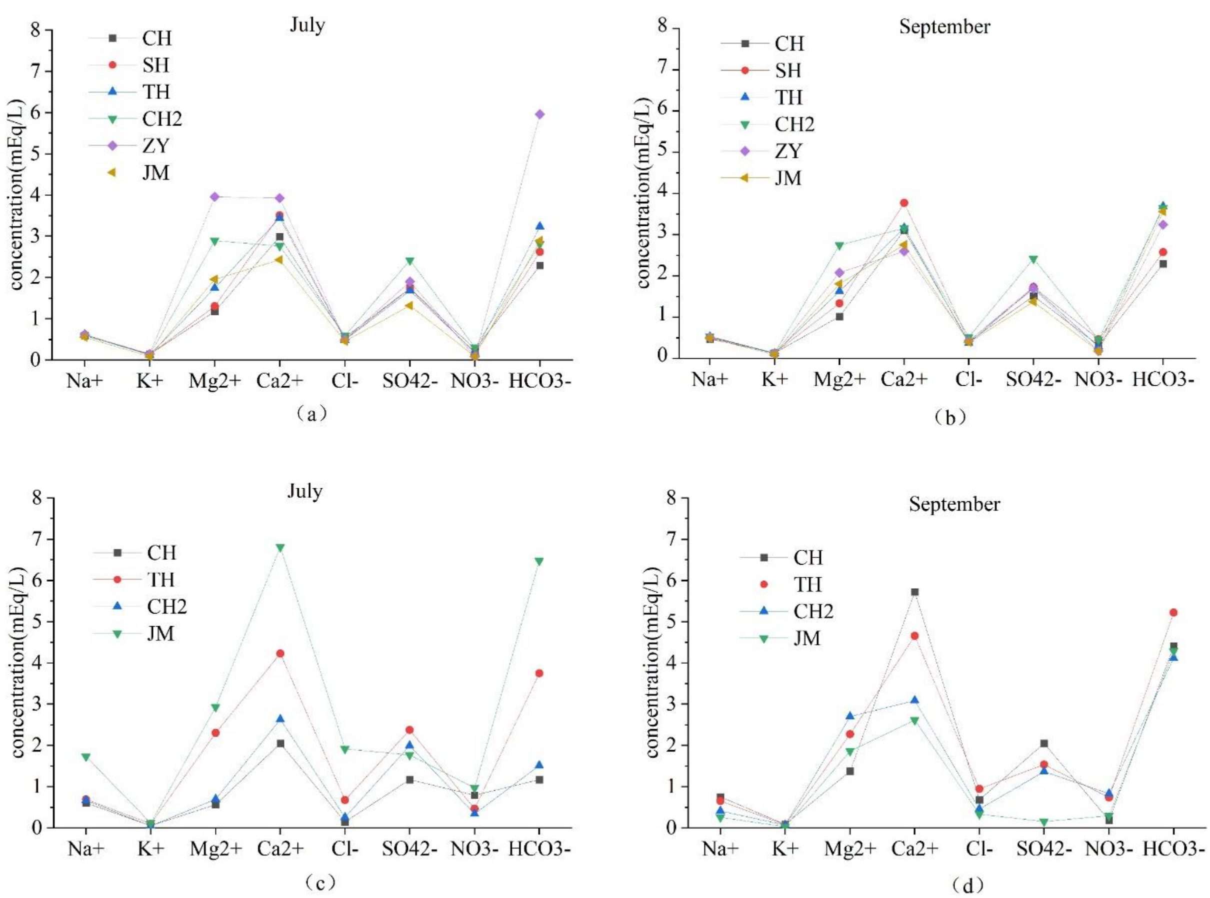

Figure 2. Average concentration of anions and cations in the surface and groundwater sampled in September 2018 and July 2019 in the mountainous watershed of Daqing River. (**a**) The average concentration of anions and cations in surface water in July; (**b**) the average concentration of anions and cations in surface water in September; (**c**) the average concentration of anions and cations in groundwater in July; (**d**) the average concentration of anions and cations in groundwater in September (CH—Ci river, SH—Sha river, TH—Tang river, CH2—Cao river, ZY—Zhongyi river, JM—Juma river).

To study the basic hydrochemical characteristics of water samples, Origin software was used to draw Piper diagrams of surface water and groundwater at different sampling periods (Figure 3). It can be seen that the surface water and groundwater in the mountain watershed of the Daqing River are mostly freshwater with low hardness, and the proportion of HCO_3^- to anions in surface water ranges from 52 to 76%, while the proportion of Ca^{2+} to cations ranges from 51 to 70% (Figure 3). Under the influence of anthropogenic activities, for example, residential sewage discharge, farmland fertilization and so on, there are differences in the chemical types of surface water in local areas, but overall, the hydrochemical characteristics of surface water and groundwater in the mountainous watershed of Daqing River basin are relatively stable, and both are dominated by HCO_3-Ca.

4.2. Isotopic Characteristic

The δD and $\delta^{18}O$ values of surface water and groundwater in different tributaries of the Daqing River Mountain basin showed different variation characteristics before and after the rainy season. According to Figure 4, the mean values of δD and $\delta^{18}O$ from two samples in each watershed range from −50‰ to −60‰ and −7‰ to −8‰, respectively. The values of δD and $\delta^{18}O$ in the CH, SH and CH2 rivers in July were higher than those in September, while the values of δD and $\delta^{18}O$ in July were lower than those in September for the TH, ZY and JM rivers.

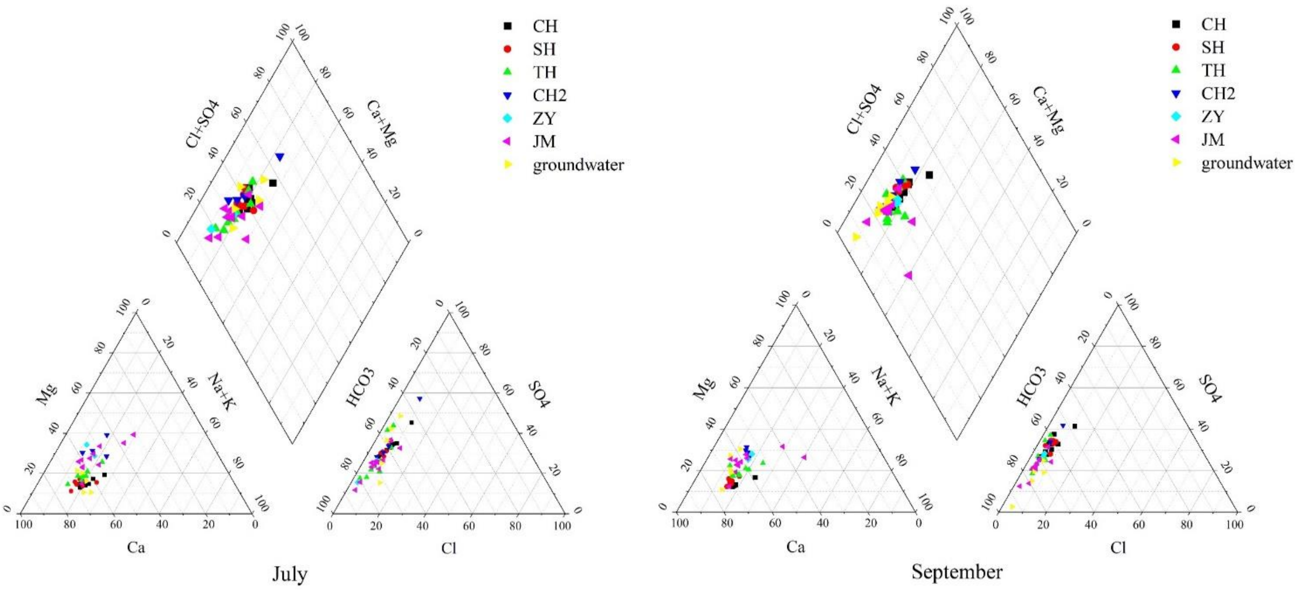

Figure 3. Chemical Piper diagram of surface water samples taken before and after the rainy season in the mountainous watershed of Daqing River (CH—Ci river, SH—Sha river, TH—Tang river, CH2—Cao river, ZY—Zhongyi river, JM—Juma river).

As for the variation characteristics of δD and δ^{18}O in the groundwater of each tributary sampled twice, there was no groundwater sample in the ZY river in September. The mean values of δD and δ^{18}O varied from −54 to −65‰ and from −7.1 to −9.3‰, respectively, for the remaining five tributaries. Specifically, for the CH, TH and CH2 rivers, the δD values in July were lower than those in September, while the δD values of the SH and JM rivers in July were higher than those in September, and the δ^{18}O values of those five watersheds in July were lower than those of September.

The correlation of δD and δ^{18}O in surface water and groundwater before and after the rainy season in the whole mountainous watershed of the Daqing River and its comparison with the atmospheric precipitation line were established. As shown in Figure 5a, compared with the global meteoric water line (GMWL), the slope of the local meteoric water line (LMWL) is 6.36, which is less than 8, and is located at the lower right of the GMWL, indicating that the evaporation in this area is stronger. The slope of the evaporation line for surface water samples in September was 4.67 times smaller than that in July (4.96), indicating that the evaporation intensity of surface water in September is stronger than that in July.

As can be seen from Figure 5b, the δD and δ^{18}O of groundwater fall to the lower left of the GMWL, basically on or near the LMWL, indicating that groundwater mainly comes from atmospheric precipitation recharge and there is some evaporative fractionation. The slope of the evaporation line in July was 5.16 lower than that in September (5.77), indicating that the intensity of evaporation of groundwater in July is greater than that in September. The fitted line of surface water and groundwater was established. For the surface water sample in July was $\delta D = 4.96\delta^{18}O - 19.41$ ($R^2 = 0.98$) and in September was $\delta D = 4.67\delta^{18}O - 22.44$ ($R^2 = 0.96$). For the groundwater sample in July was $\delta D = 5.16\delta^{18}O - 16.42$ ($R^2 = 0.98$) and in September was $\delta D = 5.77\delta^{18}O - 14.12$ ($R^2 = 0.88$).

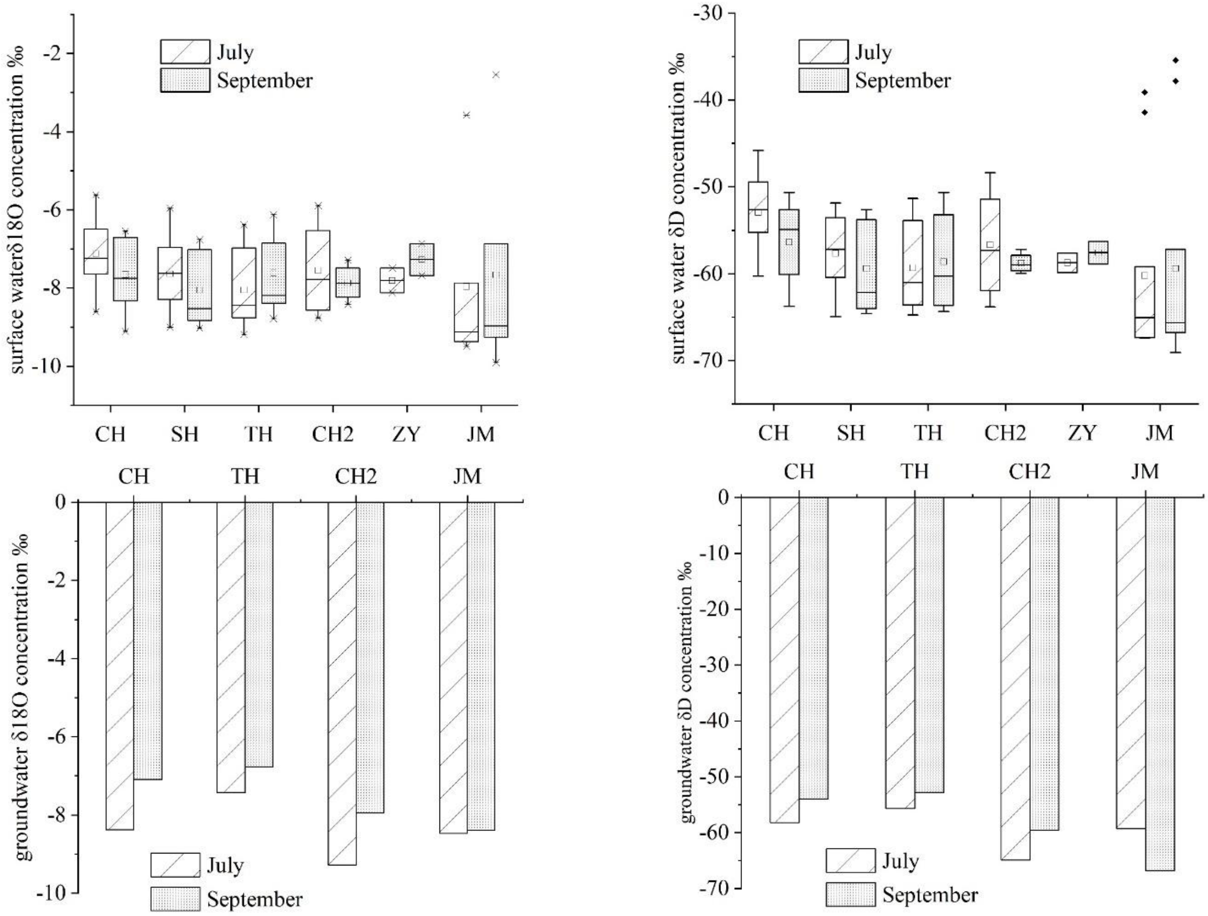

Figure 4. Distribution of δD and $\delta^{18}O$ in surface water and groundwater sampled twice in the mountainous watershed of Daqing River (CH—Ci river, SH—Sha river, TH—Tang river, CH2—Cao river, ZY—Zhongyi river, JM—Juma river).

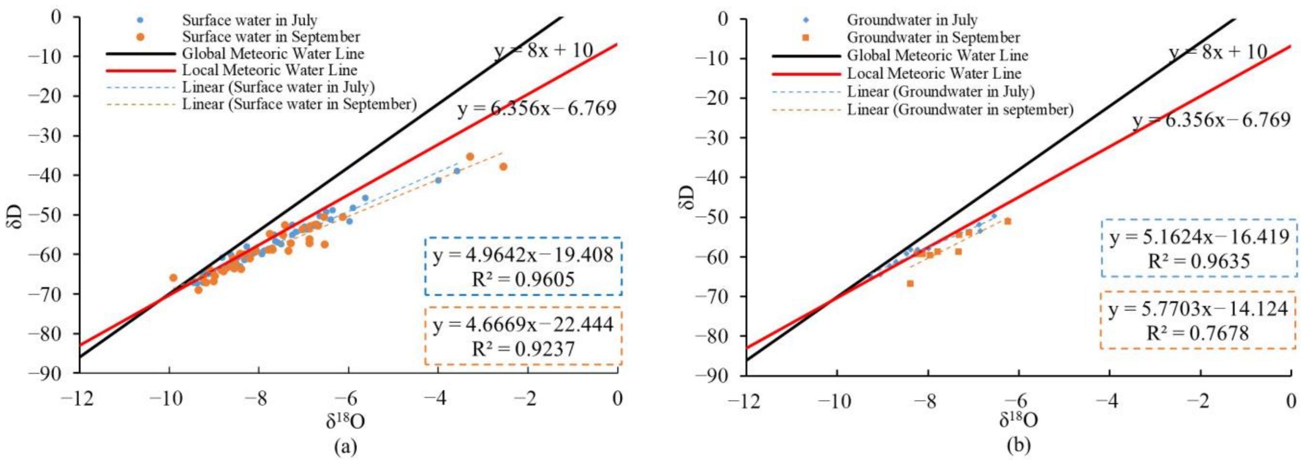

Figure 5. δD and $\delta^{18}O$ relationship between surface water and groundwater- Meteoric Water Line sampled twice in the Mountainous watershed of Daqing River.

5. Discussion

5.1. Isotopes and Chemical Characteristics of Water

At the watershed scale, hydrogen and oxygen isotopes are influenced by temperature, elevation, location, season, and recharge sources [33,34]. Through the study of water's hydrogen and oxygen isotopes, δD and $\delta^{18}O$ in the surface water and groundwater in the mountainous watershed of the Daqing River showed a good linear relationship both before and after the rainy season as previously mentioned in Section 4.2. For arid and semi-arid regions, the slope of the LMWL is lower than the GMWL, which is mainly affected by elevation and latitude. The mountain ranges make the air rise, and the landforms also play the role of cooling and condensing water vapor. The water vapor enriched with heavy isotopes will preferentially condense and land, so the higher the elevation, the lower the $\delta^{18}O$ and δD values [35–39]. For example, in the Dabie Mountains area in the upper reaches of the Huaihe River, for every 100m rise, the change in $\delta^{18}O$ is −0.13‰ in the dry season and −0.15‰ in the wet season [40]. In the Qilian Mountains, the average elevation gradient of $\delta^{18}O$ in the region was −0.26‰ $(100\ m)^{-1}$, and the elevation gradient was higher in summer than in winter [41]. Thus, to further analyze the distribution of water isotopes in the mountainous watershed of the Daqing River, the correlation between the $\delta^{18}O$ values of the two samples and the elevation of the sampling sites was plotted separately (Figure 6). The results show that, with the decrease in altitude, there is a decreasing trend of the $\delta^{18}O$ value of surface water samples, while the decreasing trend of the $\delta^{18}O$ value of groundwater samples is not obvious. In addition, the slopes of surface water and groundwater in July are 4.96 and 5.16, respectively, compared with September, which is very similar, indicating that the connection between the surface water and groundwater in the study area is stronger in July, that is, before the rainy season (Figure 6).

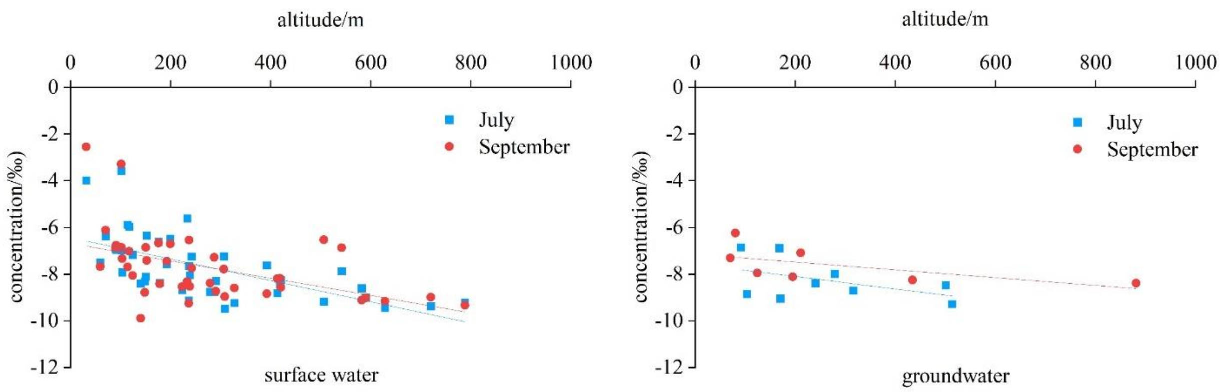

Figure 6. Relationship between δ18O and the altitude of surface and groundwater samples in the mountainous watershed of Daqing River.

Through the hydrochemical study, the two sampling results showed that the chemical types of the six rivers were mainly Ca-Mg-HCO_3 types. To further compare and analyze the concentration differences of major anions and cations in the same watershed, the concentration distribution of Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} in each watershed sampled twice was plotted (Figure 7). The results of the two samplings showed that the difference in the Ca^{2+} concentration between the two samplings was not significant, except the Ca^{2+} concentration of the ZY river in July (78.52 mg/L) was higher than in September (52.00 mg/L). Similarly, the concentration of Mg^{2+} in the ZY river in July was much higher than in September, with little difference in the rest of the five rivers: the largest was seen in the CH2 river at about 30 mg/L, and 20 mg/L was seen in the rest of the four rivers.

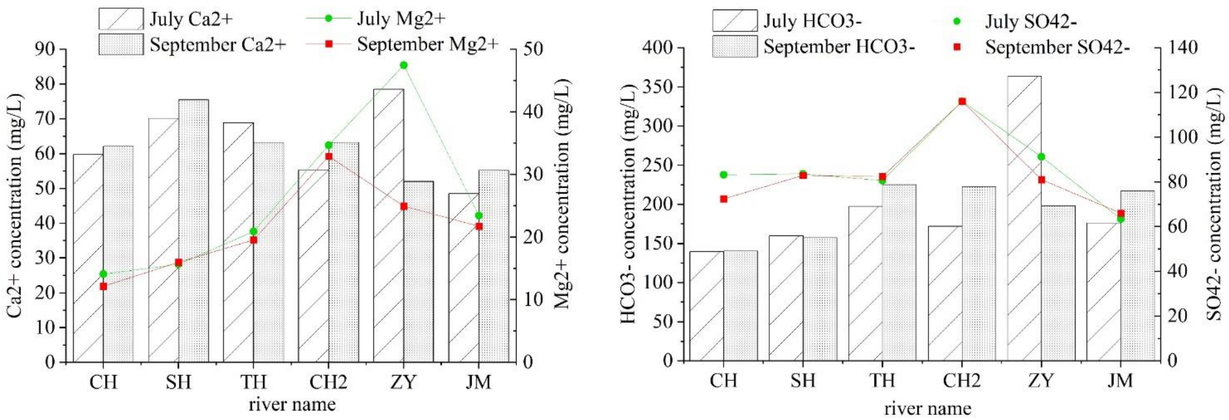

Figure 7. Average concentrations of main cations and anions in the surface water of the mountainous watershed of Daqing River (CH—Ci river, SH—Sha river, TH—Tang river, CH2—Cao river, ZY—Zhongyi river, JM—Juma river).

For HCO_3^- concentration, except for the CH and SH rivers, the difference between the other four rivers was obvious. Specifically, the difference between the two samplings at the ZY river is the largest, which was greater in July than in September, while the other three rivers all showed the characteristics of being smaller in July than in September. Thus, it seems that the water quality of the surface water in the mountainous watershed of the Daqing River is most influenced by the dilution of precipitation only in the ZY river.

5.2. Correlation between Isotopic Composition and Hydrochemical

D and ^{18}O in water are stable isotopes that make up the water molecule. When the water body's hydrogen and oxygen isotopic composition is not significantly correlated with the ion mass concentration and mineralization, the water is mainly affected by the recharge source [11]. While the hydrogen and oxygen isotope composition of the water body is significantly correlated with ion mass concentration and mineralization, the water body is subject to evaporation induced by hydrogen and oxygen isotope fractionation, which makes the hydrogen and oxygen isotope heavy, and the corresponding ion mass concentration and mineralization will increase. Therefore, the correlation between the hydroxide isotope content and the eight major ions in the common surface water and groundwater samples in two sampling times was analyzed (Table 1).

Table 1. Correlation analysis of hydrochemical and hydrogen and oxygen isotopic composition in the mountainous watershed of Daqing River.

Year	Water Type	Number	Isotope	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-
201809	surface water	42	^{18}O	−0.317 *	0.325 *	−0.014	0.351 *	0.342 *	−0.02	−0.166	−0.223
			D	−0.273	0.370 *	−0.087	0.373 *	0.380 *	0.854	0.499	0.039
	groundwater	5	^{18}O	0.867	0.767	0.049	0.934 *	0.980 **	0.799	0.153	0.811
			D	0.872	0.889 *	0.05	0.934 *	0.873	0.900 *	0.276	0.716
201907	surface water	42	^{18}O	−0.384 *	0.08	0.016	0.233	0.323 *	−0.036	−0.073	−0.269
			D	−0.333 *	0.164	−0.043	0.216	0.326 *	−0.001	−0.001	−0.288
	groundwater	5	^{18}O	0.166	0.655	0.441	−0.103	0.16	0.094	−0.177	0.303
			D	0.199	0.628	0.45	−0.015	0.208	−0.031	0.065	0.332

Note: superscript * indicates significant correlation at 0.05 level, ** indicates significant correlation at 0.01 level.

After the rainy season, the hydrogen and oxygen isotopic compositions of surface water in the mountainous watershed of the Daqing River are significantly correlated with Ca^{2+}, K^+, Na^+ and Cl^-, and the hydrogen and oxygen isotopic compositions of groundwater are significantly correlated with Na^+, Cl^-, K^+ and SO_4^{2-}, while the hydrogen and oxygen isotopic compositions of surface water before the rainy season are only significantly correlated with Ca^{2+} and Cl^-, and the hydrogen and oxygen isotopic compositions of groundwater have no significant correlation with the mass concentration of each ion. This indicates that the evaporation intensity of surface water after the rainy season is stronger than that before the rainy season, causing hydrogen and oxygen isotope fractionation.

5.3. Transformation Relationship between Surface Water and Groundwater

The transformation between surface water and groundwater is an important part of the water cycle process in the basin, and an accurate grasp of its mechanism and transformation process is the basis for the management and protection of water resources in the basin [42,43]. The slopes of the fitted lines of hydrogen and oxygen isotopes of groundwater in July and September in the mountainous watershed of the Daqing River basin (5.16 and 5.77) were higher than those of surface water (4.96 and 4.67), indicating that the groundwater and surface water in this basin are replenishing each other. The difference occurs because of the evaporative fractionation and mixing. The conversion ratio of surface water and groundwater in the mountainous watershed of the Daqing River basin can be calculated by using the two-terminal element theory (Formula 2).

There is a large gradient in the riverbed in the upper reaches of the Daqing River, and there are obvious groundwater outcrops at the source of each tributary, forming descending or ascending springs that directly replenish the river runoff and becoming the source of the main tributaries. In addition, the groundwater seeping from the mountains on both sides of the river recharges the surface water, and the river runoff increases gradually. For example, there are mountain springs exposed in the headwaters of the SH river, which has a high recharge elevation. Both before and after the rainy season, the groundwater recharges the surface water, and the recharge river water is excreted in the form of spring water; the conversion ratios are 1.6 and 50.1%, respectively. However, in the headwater areas of the TR and CR rivers, affected by topographic conditions, the surface water is recharged to groundwater through seepage measurement and infiltration. Before the rainy season, the conversion ratio of surface water to groundwater in the TR river is 6.1%, and that of the CR river after the rainy season is 50.4%. Through calculation, it can be found that the exchange of surface water and groundwater in the mountainous area of Daqing River is frequent (Figure 8).

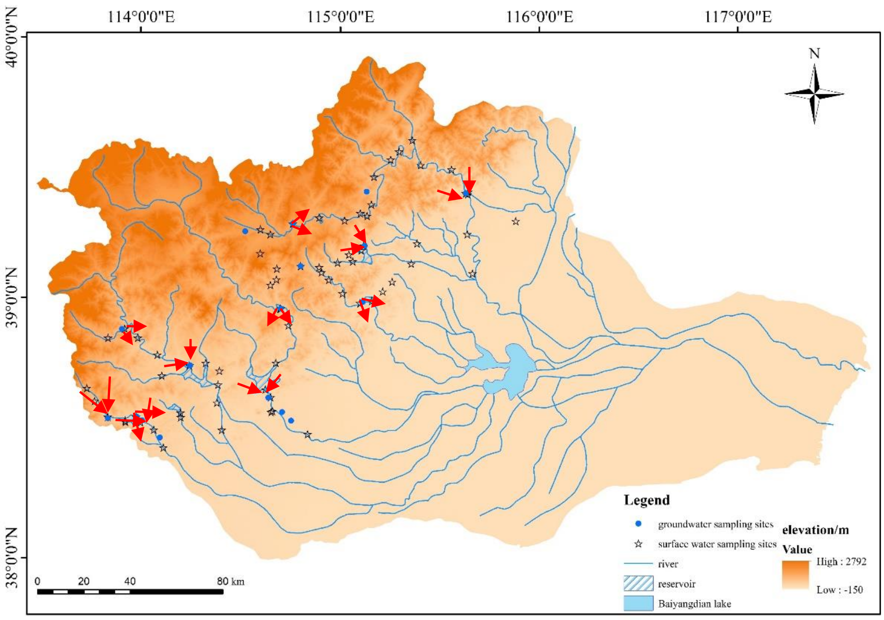

Figure 8. The relationship between surface water and groundwater transformation in the mountainous watershed of Daqing River.

After the rainy season, the exchange of surface water and groundwater is frequent, and the isotope points of surface water and groundwater are close to the meteoric water line. This can indicate that both surface water and groundwater in the mountainous watershed of the Daqing River are mainly recharged by rainfall. Therefore, it is initially determined that the declining runoff in the mountainous area is due to the continuous decline of the groundwater level in the piedmont plain. The hydraulic gradient between the mountainous area and the piedmont plain is becoming larger, the replenishment effect of the mountain transition zone to the piedmont plain is strengthened, and the mountain water resources are more often discharged downstream in the form of groundwater, which also leads to the further reduction of the surface water outcrop in the mountain area.

6. Conclusions

The hydrochemical type of water in the research basin is mainly Ca-HCO_3^-, which belongs to a group of low mineralization water, and the hydrochemical characteristics are relatively stable, indicating that the recharge source of each basin is mainly atmospheric precipitation. The $\delta^{18}O$ value of the study watershed is affected by the altitude (elevation), and the $\delta^{18}O$ value of the surface water samples has a decreasing trend with the decrease in the altitude, but the decreasing trend of the $\delta^{18}O$ value of the groundwater sample is not obvious with the decrease in the altitude.

The evaporation intensity of surface water after the rainy season is stronger than before the rainy season, and the connection between surface water and groundwater is stronger before the rainy season. At the same time, due to the influence of topographical conditions in the study area, the exchange of surface water and groundwater is frequent, and the exchange ratio before and after the rainy season is quite different: the exchange ratio after the rainy season can reach more than 50%. In addition, due to the continuous decline of the groundwater level in the piedmont plain, the hydraulic gradient between the mountainous area and the piedmont plain keeps increasing, and the recharge effect of the mountainous transition zone on the piedmont plain is strengthened. The water resources in mountainous areas are more replenishing to the downstream in the form of groundwater, and the amount of the surface water in the mountainous area further decreases.

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References

1. Hynes, H.B.N. The Ecology of Running Waters. *Ecology* **1970**, *52*, 731–732.
2. Ellen, W. *Mountain Rivers*; American Geophysical Union: Washington, DC, USA, 2000.
3. Sophocleous, M. Interactions between groundwater and surface water: The state of the science. *Hydrogeol. J.* **2002**, *10*, 52–67. [CrossRef]
4. Woessner, W.W. Stream and fluvial plain groundwater interactions. *Ground Water* **2000**, *38*, 423–429. [CrossRef]
5. Edlund, M.; Almendinger, J.; Fang, X.; Hobbs, J.; VanderMeulen, D.; Key, R.; Engstrom, D. Effects of climate change on lake thermal structure and biotic response in northern wilderness lakes. *Water* **2017**, *9*, 678. [CrossRef]
6. Alexakis, D.E.; Kiskira, K.; Gamvroula, D.; Emmanouil, C.; Psomopoulos, C.S. Evaluating toxic element contamination sources in groundwater bodies of two Mediterranean sites. *Environ. Sci. Pollut. Res.* **2021**, *28*, 34400–34409. [CrossRef] [PubMed]

7. Gamvroula, D.; Alexakis, D.; Stamatis, G. Diagnosis of groundwater quality and assessment of contamination sources in the Megara basin (Attica, Greece). *Arab. J. Geosci.* **2012**, *6*, 2367–2381. [CrossRef]
8. Alexakis, D.E. Meta-evaluation of water quality indices application into groundwater resources. *Water* **2020**, *12*, 1890. [CrossRef]
9. Gad, M.; Saleh, A.H.; Hussein, H.; Farouk, M.; Elsayed, S. Appraisal of surface water quality of nile river using water quality indices, spectral signature and multivariate modeling. *Water* **2022**, *14*, 1131. [CrossRef]
10. Wang, W.K.; Li, J.T.; Wang, Z.; Feng, X.Z.; Xu, M.; Wang, W.M.; Yang, L.J. Evolution of the Relationship between River and Groundwater and Several Scientific Problems. *J. Jilin Univ. (Earth Sci. Ed.)* **2007**, *2*, 231–238. (In Chinese with English Abstract)
11. Song, X.F.; Liu, X.C.; Xia, J.; Yu, J.J.; Tang, C.Y. Research on the transformation relationship between surface water and groundwater in the Huaisha River basin based on environmental isotope technology. *Sci. China* **2007**, *37*, 102–110. (In Chinese with English Abstract)
12. Zhang, B.; Song, X.F.; Zhang, Y.H.; Han, D.M.; Yang, L.H.; Tang, C.Y. Relationship between surface water and groundwater in the second Songhua River basin. *Adv. Water Sci.* **2014**, *25*, 336–347. (In Chinese with English Abstract)
13. Cook, P.G.; Favreau, G.; Dighton, J.C.; Tickell, S. Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers. *J. Hydrol.* **2003**, *277*, 74–88. [CrossRef]
14. Song, X.F.; Liu, X.; Xia, J.; Zhang, X.C.; Yu, J.J.; Zhang, Y.H. Interactions Between Surface Water and Groundwater in Chabagou Catchment Using Hydrogen and Oxygen lsotopes. *J. Basic Sci. Eng.* **2009**, *17*, 8–20. (In Chinese with English Abstract)
15. Zhang, Y.H.; Wu, Y.Q.; Wen, X.H.; Su, J.P. Application of environmental isotopes in water cycle. *Adv. Water Sci.* **2006**, *17*, 738–747. (In Chinese with English Abstract)
16. Bajracharya, R.; Nakamura, T.; Ghimire, S.; Man Shakya, B.; Kazi Tamrakar, N. Identifying Groundwater and River Water Interconnections Using Hydrochemistry, Stable Isotopes, and Statistical Methods in Hanumante River, Kathmandu Valley, Central Nepal. *Water* **2020**, *12*, 1524. [CrossRef]
17. Mahlangu, S.; Lorentz, S.; Diamond, R.; Dippenaar, M. Surface water-groundwater interaction using tritium and stable water isotopes: A case study of Middelburg, South Africa. *J. Afr. Earth Sci.* **2020**, *171*, 103886. [CrossRef]
18. Hao, S.; Li, F.D.; Li, Y.H.; Qiao, Y.F.; Zhu, N.; Fu, K. Transformation Between Surface Water and Groundwater in Ebinur Lake Basin Based on Hydrogen and Oxygen Stable lsotopes. *J. Soil Water Conserv.* **2021**, *35*, 172–185. (In Chinese with English Abstract)
19. Xia, J. A Perspective on Hydrological Base of Water Security Problem and its Application Study in North China. *Prog. Geogr.* **2002**, *6*, 517–526. (In Chinese with English Abstract)
20. Zhou, G.F.; Xie, W.J. Study on Meteorological Drought and Water Resource Situation of the Haihe River Basinin the Last 20 Years. *Land Resour. Inf.* **2021**, 1–5, (In Chinese with English Abstract). Available online: https://web02.cnki.net/kmobile/Journal/detail/DKCJ/GTZQ20211020000 (accessed on 20 March 2022).
21. Yao, P.; Lu, G. Hydrochemical and isotopic characteristics of the Juma River and their implications. *Environ. Sci.* **2017**, *36*, 1525–1536. (In Chinese with English Abstract)
22. Chen, Y. *Pore-Water and Groundwater Hydrochemical Characteristics and Hydrogeochemical Processes in Baiyangdian Lake Basin*; China University of Geosciences: Beijing, China, 2018.
23. Yuan, R.Q.; Song, X.F.; Wang, P.; Zhang, Y.H.; Wang, S.Q.; Tang, C.Y. Impacts of percolation in Baiyangdian Lake on groundwater. *Adv. Water Sci.* **2012**, *23*, 751–756. (In Chinese with English Abstract)
24. Sun, C.J.; Chen, W. Relationship Between Groundwater and Surface Water Based on Environmental Isotope and Hydrochemistry in Upperstream of the Haihe River basin. *Sci. Geogr. Sin.* **2018**, *3*, 790–799.
25. Yang, R.X.; Hou, B.D.; Lu, F.; Liang, C.; Zhao, Y.; Xiao, W.H. Preliminary analysis and promotion of water resources carrying capacity for Xiong'an New Area. *Water Resour. Hydropower Eng.* **2019**, *50*, 19. (In Chinese with English Abstract)
26. Sakakibara, K.; Tsujimura, M.; Song, X.F.; Zhang, J. Spatiotemporal variation of the surface water effect on the groundwater recharge in a low-precipitation region: Application of the multi-tracer approach to the Taihang Mountains, North China. *J. Hydrol.* **2017**, *545*, 132–144. [CrossRef]
27. Liu, Y.Y. *Evolution Analysis and Health Assessment of Baiyangdian Wetland Ecosystem*; Hebei Agricultural University: Hebei, China, 2019.
28. Yuan, X.M.; Liu, Q.; Ma, X.J.; Sun, Y.S.; Yan, S.R.; Li, M. Hydrochemical Characteristics and Possible Controls of the Surface Water in Baiyangdian lake basin. *Environ. Eng.* **2020**, *38*, 1–6. (In Chinese with English Abstract)
29. Yang, H.; Cao, J.S. Analysis of basin morphologic characteristics and their influence on the water yield of mountain watersheds upstream of the Xiong'an New Area, North China. *Water* **2021**, *13*, 2903. [CrossRef]
30. Clark, I.D.; Fritz, P. *Environmental Isotopes in Hydrogeology*, 2nd ed.; Taylor and Francis: Abingdon, UK; Chemical Rubber Company Press: Boca Raton, FL, USA, 1997.
31. Aiken, G.R.; Achim, A.; Amundson, R.G.; Luis, A.A.; Aravena, R.O. *Isotope Tracers in Catchment Hydrology*; Elsevier BeslotenVennootschap: Amsterdam, The Netherlands, 1998.
32. Katherine, W.D.; Eileen, P. Investigating hydraulic connections and the origin of water in a mine tunnel using stable isotopes and hydrographs. *Appl. Geochem.* **2009**, *24*, 2266–2282.
33. Dansgaard, W. Stable isotope in precipitation. *Tellns* **1964**, *16*, 436–468.
34. Allison, G.B. The relationship between 180 and deuterium in water in sand columns undergoing evaporation. *J. Hydrol.* **1982**, *55*, 163–169. [CrossRef]

35. Joussaume, S.; Sadourny, R.; Jouzel, J. A general circulation model of water isotope cycles in the atmosphere. *Nature* **1984**, *311*, 24–29. [CrossRef]
36. Siegenthaler, U.; Oeschge, R.H. Correlation of ^{18}O in precipitation with temperature and altitude. *Nature* **1980**, *285*, 314–317. [CrossRef]
37. Araguas, L.; Froe hlich, K.; Rozanski, K. Stable isotope composition of precipitation over Southeast Asia. *J. Geophys. Res. (Atmos.)* **1998**, *103*, 28721–28742. [CrossRef]
38. Ma, J.Z.; Zhang, P.; Zhu, G.F.; Wang, Y.Q.; Edmunds, W.M.; Ding, Z.Y.; He, J.H. The composition and distribution of chemicals and isotopes in precipitation in the Shiyang River system, northwestern China. *J. Hydrol.* **2012**, *436*, 92–101. [CrossRef]
39. Guo, X.Y.; Feng, Q.; Wei, Y.P.; Li, Z.X.; Liu, W. An overview of precipitation isotopes over the extensive Hexi Region in NW China. *Arab. J. Geosci.* **2015**, *8*, 4365–4378. [CrossRef]
40. Zhang, P. *Hydrogen-Oxygen Isotope Geochemistry and Environmental Indication of River Water in the Dabieshan Area, the Upper Watershed of Huaihe River, China*; China University of Geosciences: Beijing, China, 2019.
41. Ma, X.G.; Jia, W.X.; Zhu, G.F.; Ding, D.; Pan, H.X.; Xu, X.T.; Guo, H.W.; Zhang, Y.; Yuan, R.F. Stable isotope composition of precipitation at different elevations in the monsoon marginal zone. *Quat. Int.* **2018**, *493*, 86–95.
42. Kallbus, E.; Reinstorf, F.; Schirmer, M. Measuring methods for groundwater-surface water interactions: A review. *Hydrol. Earth Syst. Sci.* **2006**, *3*, 873–887. [CrossRef]
43. Ochoa, C.G.; Sierra, A.M.; Vives, L.; Zimmermann, E.; Bailey, R. Spatio-temporal patterns of the interaction between groundwater and surface water in plains. *Hydrol. Processes* **2020**, *34*, 1371–1392. [CrossRef]