

Study on Geochemical Evolution and Isotopic Characteristics of Groundwater in Arid and Semi-arid Areas



Lishu Wang, Qingjiao Cao, Yunxin Zhang, Fei Liu, Yingying Shen, Qiang Ma and Yunpu Zheng

Abstract The utilization ratio of water resources is remarkably high in the Shiyang River Basin, which is a typical zone susceptible to water resources crisis in the arid area in China. Owing to the continuous deterioration of the ecological environment in the Shiyang River Basin, it is of great significance to investigate the groundwater circulation and geochemical evolution law in this area. Samples were collected from the top of the Qilian Mountains to Hongyashan Reservoir along the flow cross section. Isotopic survey and geochemical technology were employed to analyze hydrochemistry and environmental isotopes of precipitation, surface water and groundwater. Results indicated that precipitation was the provenance of water resources in the Shiyang River Basin. The groundwater runoff system accepted river leakage and irrigation water infiltration recharge constantly in the process of the runoff to the downstream, meanwhile drained through the river overflow and pumping with a primary vertical movement. The downstream of the Basin was the main groundwater discharge area. The groundwater in the northern Basin

L. Wang · Q. Cao · Y. Zhang · F. Liu · Y. Zheng (✉)
School of Water Conservancy and Hydropower, Hebei University of Engineering,
178 S. Zhonghua Street, Handan 056021, Hebei, China
e-mail: zhengyunpu_000@sina.com

L. Wang
e-mail: fc8232@126.com

Q. Cao
e-mail: 13931061206@163.com

Y. Zhang
e-mail: zyx14315@163.com

F. Liu
e-mail: liufei@hebeu.edu.cn

Y. Shen
China Irrigation and Drainage Development Center, Beijing 100000, China
e-mail: shenyinying_cugb@163.com

Q. Ma
Yahoo! Inc., 701 1st Ave, Sunnyvale, CA 94089, USA
e-mail: qiang@yahoo-inc.com

overflowed into the surface water due to the basement uplift. The TDS (Total Dissolved Solids) values were between 131 and 1750 mg/L, gradually increasing along the flow direction. The hydrochemical types showed an obvious zonation from the upper reaches to the lower, which gradually changed from bicarbonate to sulphates.

Keywords Environmental isotopes · Hydrochemistry · Groundwater circulation Wuwei Basin

1 Introduction

The Shiyang River Basin, located in the eastern part of the Hexi Corridor in the middle of Gansu province, Northwestern China, is considered a typical arid and semi-arid area. As a result of the long-term water resources development in the Basin, the Shiyang River Basin has become one of the most over-exploited inland basins. Water resources shortage is an increasingly serious issue in China, especially in the arid and semi-arid areas of the northwest. The Shiyang River is an eco-environmentally fragile area, which is characterized by low and irregular rainfall, high temperatures and evaporation, and notable drought periods [1]. In such arid and semi-arid environment, groundwater is a significant part of the total water resource and plays a key role as a water supply for drinking and irrigation [2].

Research interests have been focused on aspects such as utilization survey, evolutionary prediction, reserve estimation and systematic assessment of natural water resources. Some reasonable allocation and utilization plans have been proposed [3]. The effective development and management of the valuable groundwater resources in the area require a better understanding of hydrochemical characteristics of the groundwater and its evolution under natural water circulation processes. During the last thirty years, environmental isotopic techniques have been commonly and largely used in the overall domain of water resources development and management [4].

The application of these relatively new techniques in the case of arid and semi-arid zones has proved to be an attractive tool for the quantitative evaluation of groundwater systems [5]. However, comprehensive approaches to groundwater understanding using chemical and isotopic indicators are relatively few, although there are several investigations on the interaction and mechanism among surface water, groundwater and rocks in recent years [6–9].

The systematic analysis of the hydrochemical types and features of the whole river basin were combined using computer simulation and isotopic geochemical methods in this study. The objective was to elucidate the controls of groundwater quality evolution, recharge, circulation and mixing processes and, furthermore, to explain the mechanism of these processes from the standpoint of environmental geochemistry. The results of the study may provide a theoretical basis for the government to make utilization strategies for water resources and development

policies in northwest China in the new century. The purpose of this paper is, thus, to make a new assessment of the availability of groundwater resources in the Wuwei Basin as the typical area of arid northwestern China based on a better understanding of hydrogeological features.

2 Geology and Hydrogeology of the Study Area

The Shiyang River Basin, located in the eastern part of Hexi Corridor in the middle of Gansu province, is a typical arid and semi-arid area (Fig. 1). The Shiyang River originates from Lenglongling Glacier of the Qilian Mountains, and ends gradually in the Tengger Desert. The Qilian Mts. form the southern part of the Basin. Many modern glaciers are distributed above 4500 m. The middle and northern part of the Basin is a plain that can be divided into two sub-basins (i.e., Wuwei Basin and Mingqing Basin).

Most of the basin belongs to the arid climate zone. Solar radiation is strong and sunny. Summer is hot and short, while winter is cold and long. The temperature difference is extremely significant. Less rainfall and evaporation intense lead to dry air.

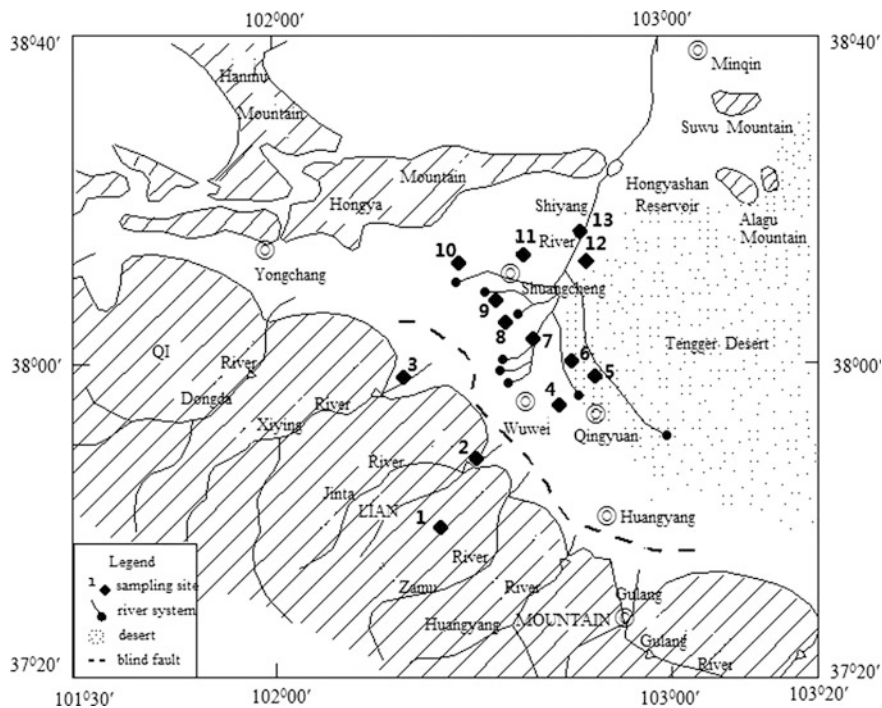


Fig. 1 Geographic location of the study area and water quality sampling point

The annual precipitation is 200–800 mm, while the evaporation capacity is 2000–3000 mm.

Consisting of Quaternary alluvial and pluvial sediments, the Wuwei Basin lies in a depression at the foot of the Qilian Mts. with an elevation ranging from 1400–2500 m. The loose Quaternary sediments filling the basin are of great thickness, which provide an ideal place for groundwater preservation. In terms of the hydrogeological characteristics, two geomorphologic units are recognized in the Wuwei Basin, a faulting terrace zone and its sub-basin. The former is in the vicinity of Qilian Mts. and lies on the head of a pluvial fan. The aquifer there is composed of gravel and sand. Well-connected porosity of the aquifer provides a good conduit for groundwater flow, which is the basin's recharge region. The sub-basin is the enrichment zone of the groundwater. As the grain size of the aquifer gradually decreases from south to north and the flow rate becomes slower, the hydraulic gradient becomes smaller. Along with the uplifting of the Quaternary basement, the burial depth of the aquifer becomes shallower, resulting in the springs of groundwater from the middle part of the Wuwei Basin (Fig. 2).

In the southern part of the Wuwei Basin, the diluvial aquifer is formed from highly permeable cobble and gravel deposits that are between 200 and 300 m thick. The aquifer specific capacity is about $3\text{--}30 \text{ l}\cdot\text{s}^{-1}\cdot\text{m}^{-1}$, and aquifer permeability is up to $100\text{--}600 \text{ m}\cdot\text{d}^{-1}$ [10]. This allows a large amount of surface runoff in the piedmont fan to seep down and recharge the aquifer. From the northern edge of this diluvial fan, the aquifer, comprising interbedded cobble gravel, fine sand and clay, becomes confined or semi-confined with piezometric levels less than 5 m depth. In many places the ground-water overflows as springs and re-emerges as streams.

The limited precipitation in the plains of the river basin accounts for less than 7% of the total ground-water recharge. Hence, as found in other inland river basins in arid northwest China [11], the aquifer in Shiyang River Basin to a large extent is

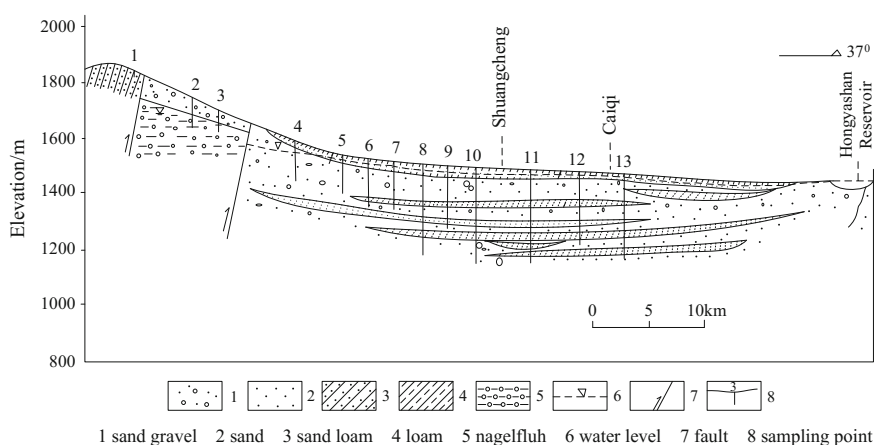


Fig. 2 Geologic section of the Wuwei Basin

recharged by surface water via river infiltration, canal system seepage and farmland irrigation water seepage. In other words, surface water and groundwater are integrated in the middle and lower basins, and the upper, middle and lower reaches are united in using water resources. The water resources in the different parts of the basin are inseparably linked: the ground-water resources in the plain area are recharged from precipitation in the Qilian Mountains. From the Qilian Mountain reach to the Hongyashan section, groundwater and surface water are closely linked due to the gradient and the uniquely permeable nature of the sediments near to the mountains. To a large extent, the groundwater is transferred back to surface water before flowing out of the section. Surface water in the Hongyashan reservoir, therefore, mainly comes from surface water and spring water originally present as short residence time ground-water within the Wuwei Basin.

3 Materials and Methods

According to the topography, geomorphology and hydrogeology, 13 groups of sampling locations from Qilian Mountain to Hongyashan Reservoir were chosen (Fig. 1). The sample points were positioned using GPS locator. The well depth, latitude, longitude, groundwater depth, water temperature as well as PH value (pH) were measured, respectively, on the scene. Sample bottles were washed three times with water sample before collecting water samples. All water samples were packed in plastic bottles, which were then sealed with wax. No air bubbles were allowed in the bottles to avoid exchanging with carbon dioxide in the air.

Precipitation materials were collected from the global precipitation isotope which was established by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). Ca^{2+} , Na^+ , K^+ , Mg^{2+} , SO_4^{2-} , Cl^- and NO_3^- were measured using Ion Chromatograph. Deuterium (D) and oxygen-18 (^{18}O) were measured by MAT-252 mass spectrometry. Hydrogen samples were prepared by the zinc reduction method under temperatures of up to 700 °C, and ^{18}O samples by a $\text{H}_2\text{O}-\text{CO}_2$ equilibrium method. Here, SMOW (standard mean ocean water) was adopted as the criterion for measuring H and O isotopic compositions. Duplicate analyses of δD and $\delta^{18}\text{O}$ were within $\pm 1\%$ and $\pm 0.1\%$, respectively.

4 Results and Discussion

4.1 Hydrochemical Characteristics of Groundwater

The hydrochemical properties of groundwater samples collected from the Quaternary aquifer system are shown in Table 1.

Table 1 TDS and isotope analysis results of water samples in the study area

Number	Site	Type	PH	TDS (mg/L)	$\delta^{18}\text{O}$ (‰)	δD (‰)
I	Wuwei1	Rain	7.1	59.3	-1.662	-22.95
II	Wuwei2	Rain	7.2	56.7	-2.45	-25.16
III	Gulang	Snow water	6.9	69.9	-8.6	-56.74
IV	Hongyashan	Surface water	-	-	-3.1	-27
1	Qilianshan	Snow water	5.5	131	-11.99	-76.7
2	Nanyingshuiku	Surface water	6.0	171	-10.35	-70.1
3	Xiyingshuiku	Surface water	6.5	444	-	-
4	Shiyanzhan	Groundwater	7.0	385	-	-
5	Dawancun	Groundwater	6.0	1063	-9.6	-64.5
6	Gaougoucun	Groundwater	6.0	1480	-9.21	-61.1
7	Yujiawancun	Groundwater	6.0	313	-9.71	-62.8
8	Hongshuihecun	Groundwater	6.5	467	-9	-60.5
9	Baiyuncun	Groundwater	5.5	906	-8.61	-56
10	Qijiahucun	Groundwater	6.0	1750	-8.4	-58.3
11	Xigoucun	Groundwater	6.5	455	-9.4	-63.2
12	Liuquancun	Groundwater	6.5	987	-9.51	-62.3
13	Caiqi	Surface water	6.0	1297	-9.69	-61.4

Note The date of I-IV from IAEA

The pH value in groundwater ranged from 5.5 to 7.0 with an average value of 6.2. The total dissolved solids (TDS) of groundwater varied from 313 to 1750 mg/l with an average of 769 mg/l. The plot of chemical analyses on a trilinear diagram of groundwater and surface water is shown in Fig. 3.

Based on the long-term observation of groundwater hydrochemistry, the hydrochemical types showed an obvious zonation from the upper to lower reaches. It changed from HCO_3^- through to SO_4^{2-} to Cl^- types (Fig. 3). As shown in Fig. 4, HCO_3^- - Ca^{2+} or HCO_3^- - Ca^{2+} - Mg^{2+} water was mainly to the south of the basin where the recharge zone was located. Meteoric water can easily flow through the gravel and pebble aquifer, and groundwater was actively circulated. As a result, the water-rock reaction time was short, which led to the formation of weakly mineralized hydrocarbonate water. From the south to the middle, the hydrochemical zone gradually transformed into a HCO_3^- - SO_4^{2-} - Ca^{2+} - Mg^{2+} or HCO_3^- - SO_4^{2-} - Ca^{2+} - Mg^{2+} - Na^+ type. Discontinuous SO_4^{2-} - HCO_3^- - Ca^{2+} - Mg^{2+} zone or even SO_4^{2-} - Ca^{2+} - Mg^{2+} water existed in the north of the basin. As a result of runoff leakage, a narrow HCO_3^- - Ca^{2+} or HCO_3^- - Ca^{2+} - Mg^{2+} zone occurred along the bank of Shiyang River. This kind of regional zonation was consistent with the flow direction of the groundwater. A hydrocarbonate (fresh water) zone was located in the south, hydrocarbonate-sulfate (fresh water) zone in the middle, sulfate-hydrocarbonate (sub-fresh water) zone in the north and a sulfate (saline water) zone in the northern margin of the basin.

The variation of TDS concentration in groundwater illustrated that the extent of groundwater-surface water interaction governed groundwater quality in the

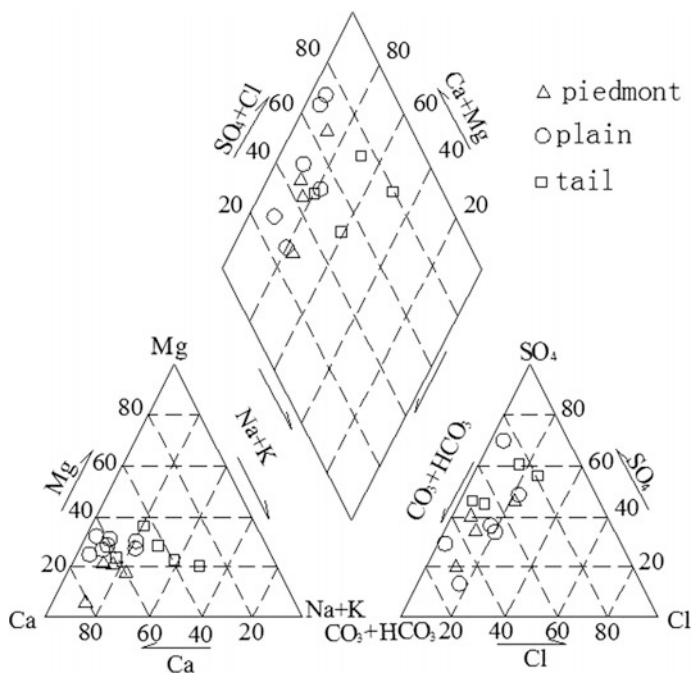


Fig. 3 Piper plot of chemical analysis of groundwater and surface water samples

Wuwei Basin (Fig. 5). The groundwater samples were collected near the river bank, allowing groundwater to be easily recharged from the river, and assuring a high quality of groundwater. Comparatively, for those collected farther from the river, the TDS and concentrations of the major ions generally rose along the flow path of the groundwater, which may be due to its greater residence time in the rock formations bearing it and the absence of the influence of surface water recharge.

4.2 Isotopic Composition of Groundwater

Hydrogen (H) and oxygen (O) are two widespread elements in nature. They have lower atomic orders and a much larger difference in isotopic ratio; that is, $\Delta A/A$ of H: D up to 100% and $^{16}\text{O}:^{18}\text{O}$ to 12.5%, where A is the mass number of the isotope and ΔA is the difference between the light and heavy isotope. The utmost isotopic fractionation can take place in natural status between their isotopes. In a natural water body, the fractionation processes of H and O isotopes were also affected by physical and chemical factors. Therefore, they were sensitive to isotopic tracers, and were widely applied in studying natural water circulation and groundwater movement [12].

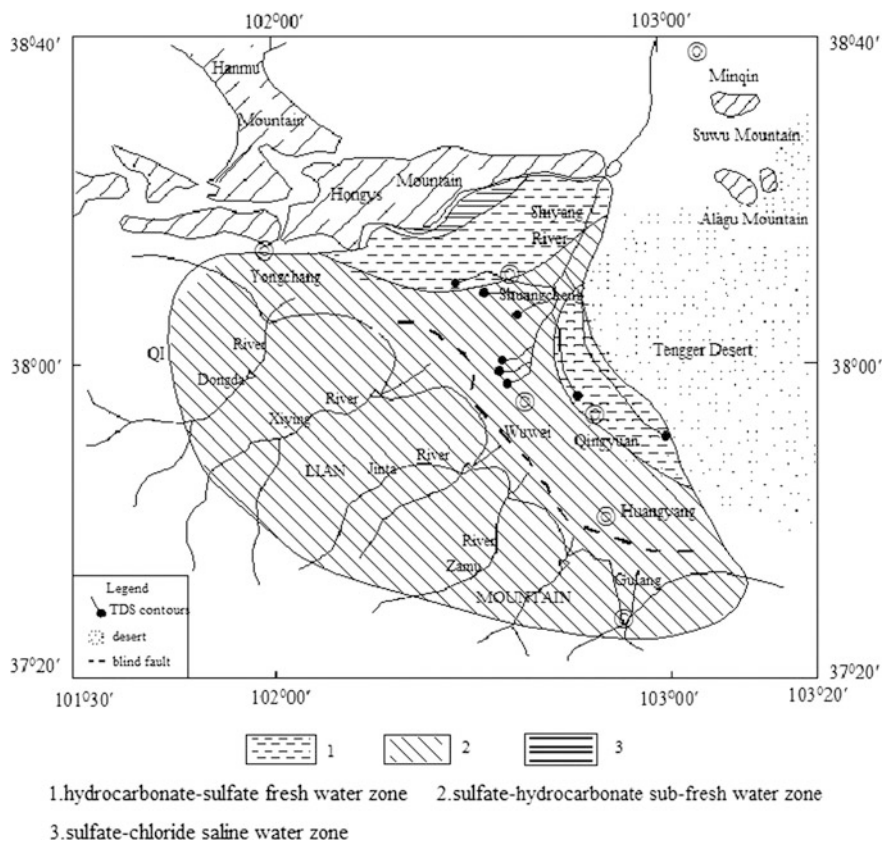


Fig. 4 Hydrochemical zones of the groundwater system in the Shiyang River

The results of stable isotope analysis both for water samples in the basin and precipitation collected in the IAEA were plotted in Fig. 6. Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation varied from -20.6 to 3.8‰ and from -158 to 33.1‰ , respectively, but they are linearly similar to the global meteoric water line (GMWL) with an equation of $\delta^2\text{H} = 7.8\delta^{18}\text{O} + 5$ ($r^2 = 0.92$), which is defined as local meteoric water line (LMWL). These values were slightly enriched and indicated modification due to evaporation in the monsoon rains producing departure from the GMWL. Weighted mean rainfall values lied around $\delta^{18}\text{O} -7.3\text{‰}$ and $\delta\text{D} -46.9\text{‰}$. These values were most likely to be the representative of the present local waters.

It showed some deviation of H and O isotopic compositions from the meteoric water line. This was mainly because of the effect of local variations in rainfall. In addition, the poor coverage of vegetation in the Shiyang River Basin was another influencing factor. when the meteoric water recharged into groundwater, drastic evaporation can produce a much larger isotopic fractionation and cause the deviation from the meteoric water line.

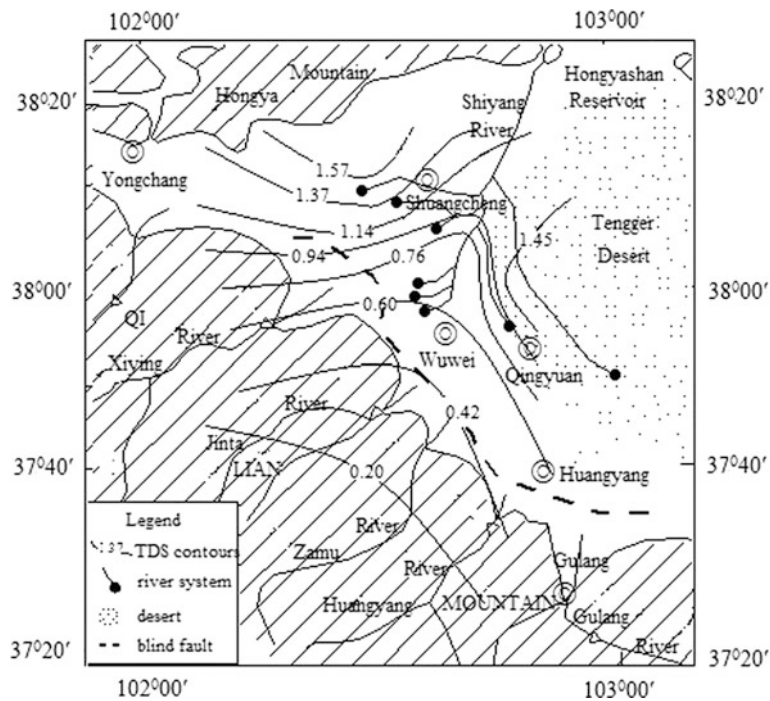


Fig. 5 TDS contours of groundwater in the study area

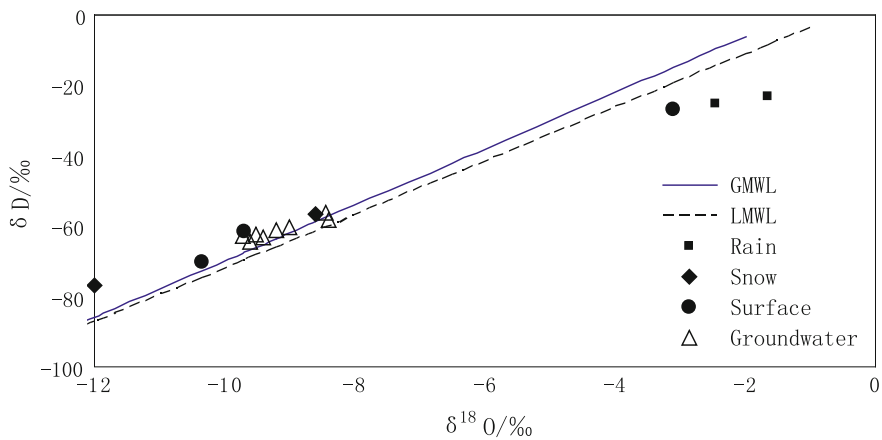


Fig. 6 Plot of $\delta^{18}\text{O}$ and δD for groundwater from the Quaternary aquifer system of the Shiyang River with plots of the GMWL and LMWL

In the vicinity of Qijiahu, the ^{18}O value was lighter than that of other areas. It may be caused by the distribution of granite and metamorphic rocks. When groundwater contacts with those rocks, water can exchange H and O isotopes with minerals in rocks. Such a water-rock equilibrium fractionation can reduce the content of ^{18}O in water. The isotopic fractionation intensity and the water-rock system depended on the temperature, quantity ratio of water and rock, and reaction time. The water-rock equilibrium fractionation was very small during groundwater leakage. The slow groundwater circulation rate enabled a full isotopic exchange between water and rock.

For the stable isotope composition of the Shiyang River running course, the mean values of $\delta^{18}\text{O}$ increased along the river course. The $\delta^{18}\text{O}$ and δD values for these samples ranged from -11.99 to -8.4‰ and from -76.7 to -56‰ , respectively (Table 1). Figure 5 illustrated that the samples from the Shiyang River running course had the similar stable isotope compositions to those from the wells drilling into the unconfined aquifers near the river bank. This indicated that evaporation probably occurred in channels, reservoirs and fields in the study area.

The majority of the isotope compositions of the groundwater samples plot were close to the GMWL (Fig. 6). This indicated that the groundwater recharge resource mainly originated from precipitation and was weakly affected by evaporation. These more depleted signatures were considered to be from the late Pleistocene and Holocene periods, during which the climate was wetter and colder than that of the present day.

4.3 Analysis on the Evolution of Groundwater Circulation

The surface runoff was converged as the atmospheric precipitation down to the surface. It infiltrated into the underground along the mountain rock of fracture and fault fracture zone to supply the groundwater. The mountainous rivers flowed into Wuwei Basin and formed pluvial and alluvial fan belt in the southern piedmont of the basin. The quaternary unconsolidated sediments varied significantly in thickness, and it was mainly composed of sandy gravel and sand gravel with great permeability. Piedmont plain rivers and irrigation water leakage, as well as the canal system were a primary source to supply the groundwater. Because the basin downstream was the main location of the groundwater evaluation, the block water boundary was constituted in the north of the basin where the bedrock exposed. Thus, the groundwater cannot directly flow into the basin downstream, whereas overflow as the basement raise, and finally transformed surface water flowing into the lower basin.

The evolution of groundwater circulation determined the characteristics of groundwater chemical and isotopic distribution in the Shiyang River Basin. TDS and hydrogen and oxygen stable isotope values increased in the flow directions. The groundwater salinity was higher, and water quality was worse with gradually closing to the lower of the downstream. Hydrochemical and isotopic distribution can clearly reflect the relationship among the groundwater (Figs. 7 and 8). TDS and oxygen isotope value gradually decreased with the increasing of depth, which obviously

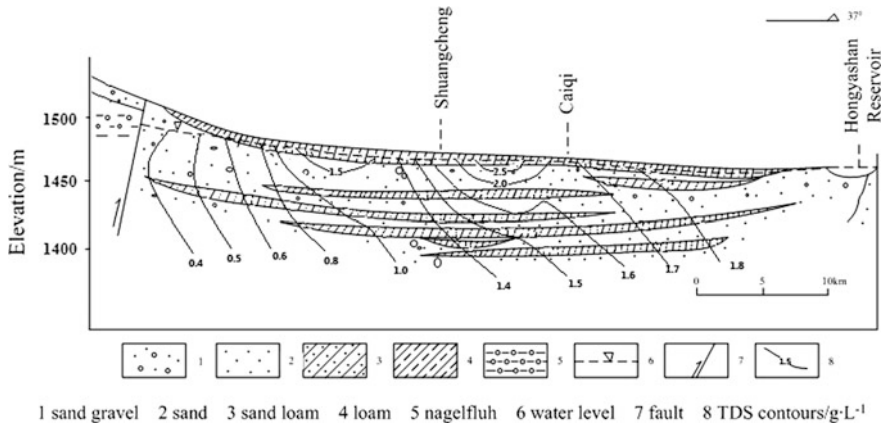


Fig. 7 TDS contours of groundwater in the study area

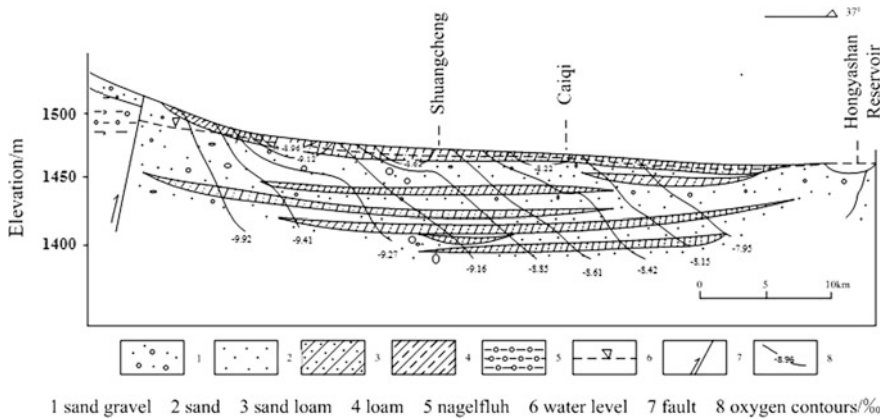


Fig. 8 $\delta^{18}\text{O}$ contours of groundwater in the study area

reflected the characteristics of groundwater laterally flowing. Groundwater of the basin flowed to the Hongyashan Reservoir and the desert area that located in the north boundary, which had the same flow law with groundwater flow field.

In the piedmont area, due to the replenishment of rainfall and runoff, groundwater was leached ceaselessly; therefore, the groundwater quality was relatively good and most of the underground water were fresh water resources, with small TDS and $\delta^{18}\text{O}$ values, TDS in 400–800 mg/L, and $\delta^{18}\text{O}$ in -9.92 to -9.27‰ . In the plain area, due to the influence of evaporation and irrigation, TDS and $\delta^{18}\text{O}$ values increased continually which resulted in the relatively high contents of TDS and $\delta^{18}\text{O}$ in some areas. For example, the content of TDS and $\delta^{18}\text{O}$ began to increase in the regions of Qingyuan, Shuangcheng and Caiqi. These regions had influence on

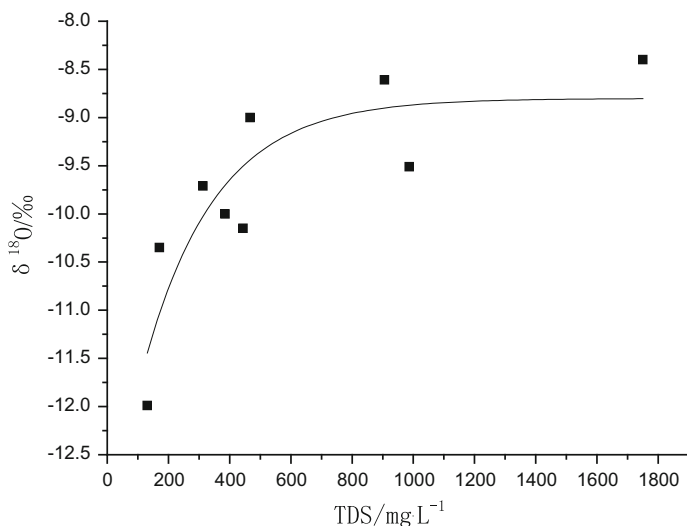


Fig. 9 Major ions versus $\delta^{18}\text{O}$ in the study area

TDS and $\delta^{18}\text{O}$ value variation trends because they were the main areas for crop planting with frequent irrigations.

TDS and isotope generally had the same changing trends. Isotope value increased with increasing TDS along the flow direction. However, this trend can probably be affected by other factors in the groundwater circulation process. Figure 9 showed that isotope firstly rapidly increased and then gradually slowed down with the increase of TDS. TDS content increased from 200 to 1000 mg/L and isotope $\delta^{18}\text{O}$ value increased quickly from the piedmont area to the middle area, which illustrated that evaporation and water-rock could greatly affect the isotope fractionation in the piedmont area and had little effect on the content of TDS. When the TDS > 1000 mg/L in the middle area, the isotope value grew slowly, and TDS value increased rapidly, which showed that the exploiting of groundwater and recharge had significantly effect on TDS but had negligible effect on isotope fractionation. This is probably due to the supply of the deep confined water with lower isotope value and irrigation and permeability of the surface water.

5 Conclusions

The hydrochemical and isotope investigation was conducted in the Wuwei Basin to understand the geochemical evolution and the residence time of the groundwater. The main conclusions are as follows:

- (1) Hydrochemical characteristics of the groundwater in Shiyang River Basin showed apparent zonation from the south to north. Hydrocarbonate-type water occurred in the gravel-pebble zone of the mount front, and sulfate-type water was mainly distributed in the alluvial, pluvial and lacustrine plain in the middle reach. Sulfate-chloride-type water appeared in the marginal area of Tenggeli Desert in the lower reach, and even chloride-type brine existed in some parts of the lower reach area.
- (2) Local meteoric water line (LMWL) equation of the Shiyang River Basin was $\delta^2\text{H} = 7.8\delta^{18}\text{O} + 5$ ($r^2 = 0.92$), which was similar to the global meteoric water line (GMWL). In the basin plain, $\delta^{18}\text{O}$ in -8.61 to -9.71% , δD in -56 to -62.8% , isotope values increased along the flow direction. This is mainly because of evaporation caused by isotope enrichment.
- (3) Precipitation was the main factor that controlled the groundwater hydrochemistry of the Wuwei Basin, whereas drastic evaporation influenced the geochemistry of the Wuwei Basin. Most of the groundwater isotopic compositions of O and H were meteoric water features, indicating that rainwater was the main recharge source to the groundwater system.
- (4) Coarser aquifers of distributing in the south of the Wuwei Basin enabled rapid recharge into groundwater. In the middle-lower reaches, the recharge rate was much slower, and it had a long circulation period. The formation of some of the groundwater was closely related to the mixing of the crevice water and brine.

Acknowledgements This study was sponsored by Natural Science Foundation of China (91125017) and Natural Science Foundation of Hebei (E2015402128).

References

1. Edmundes, W.M., Ma, J.Z., Aeschbach, H.W., et al.: Groundwater recharge history and hydrogeochemical evolution in the Minqin Basin, North West China. *Appl. Geochem.* **21**, 2148–2170 (2006). <https://doi.org/10.1016/j.apgeochem.2006.07.016>
2. Ding, Z.Y., Ma, J.Z., Zhang, B.J., et al.: Analysis on the climate change in the Shiyang River Basin since resent 50 years. *Arid Zone Res.* **24**(6), 779–784 (2007)
3. Liu, F.J., Bai, S.F., Cheng, G.D.: Utilization and exploitation of water resources and impact of human activities in Shiyang River catchment, Hexi Corridor, Gansu. In: Li, J.J., Cheng, G.D. (eds.) *Papers on the Western Resources and Environment and Sustainable Development* (in Chinese with English summary), pp. 74–82. Lanzhou University Press, Lanzhou (1998)
4. Fritz, P., Fontes, J.C.: *Handbook of Environmental Isotope Geochemistry*. Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York (1980)
5. IAEA: Arid zone hydrology: investigations with isotope techniques. In: *Proceeding of an Advisory Group Meeting, International Atomic Energy Agency, Vienna*, p. 265 (1980)
6. Shi, J.A., Wang, Q., Chen, G.J., et al.: Isotopic geochemistry of the groundwater system in arid and semiarid areas and its significance: a case study in Shiyang River Basin, Gansu Province, Northwest China. *Environ. Geol.* **40**(4–5), 557–565 (2001)
7. Feng, Q., Wei, L., Su, Y.H., et al.: Distribution and evolution of water chemistry in Heihe River Basin. *Environ. Geol.* **45**, 947–956 (2004). <https://doi.org/10.1007/s00254-003-0950-7>

8. Zhang, Y.H., Wu, Y., Su, J., et al.: Groundwater replenishment analysis by using natural isotopes in Ejina Basin, northwestern China. *Environ. Geol.* **48**, 6–14 (2005). <https://doi.org/10.1007/s00254-004-1214-x>
9. Zhu, G.F., Li, Z.Z., Su, Y.H., et al.: Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China. *J. Hydrol.* **333**, 239–251 (2007). <https://doi.org/10.1016/j.jhydrol.2006.08.013>
10. Ma, J.Z., Wang, X.S., Edmunds, W.M.: The characteristics of ground-water resources and their changes under the impacts of human activity in the arid Northwest China—a case study of the Shiyang River Basin. *J. Arid Environ.* **61**, 277–295
11. Ma, J.Z., Gao, Q.Z.: Groundwater vulnerability and its assessing method in the arid land of NW China. *Arid Land Geogr.* **26**(1), 44–49 (2003)
12. Gu, W-z., Pang, Z-h., Wang, Q-j. et al.: *Isotope Hydrology*, pp. 105–107. Science Press, Beijing (2011)