Environ Earth Sci (2015) 73:1901–1915
DOI 10.1007/s12665-014-3719-2

ORIGINAL ARTICLE

Using hydrochemical and isotopic data to determine sources of recharge and groundwater evolution in an arid region: a case study in the upper–middle reaches of the Shule River basin, northwestern China

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Received: 20 March 2014 / Accepted: 15 September 2014 / Published online: 4 October 2014

Abstract Understanding sources of recharge and mechanisms for hydrogeochemical evolution of groundwater in the Shule River basin, an arid inland river basin in northwestern China, is essential for successful water resource management. Sources of water and associated groundwater recharge processes were investigated using hydrogeological, hydrogeochemical, and isotopic methods. The study area was divided into three parts: Changma, the Shule valley, and the Beishan area. The hydrogeochemical and isotopic analysis results show that groundwater in Changma mainly originated from precipitation in the Qilian Mountains. Lateral flow from Changma is the primary recharge mechanism, while direct recharge by infiltration of precipitation can be neglected in the Shule valley. Minerals within the aquifer material (e.g., halite, calcite, dolomite, and gypsum) dissolve into water that recharges the groundwater system. Therefore, strong linear relationships were found between Na^+ and Cl^- and between $Ca^{2+}+Mg^{2+}$ and $SO_4^{2-}+HCO_3^-$, with stoichiometry ratios of approximately 1:1 in both cases. Groundwater quality in the region is generally good, with low salinity and hardness. Local precipitation is the only source of recharge for groundwater in the Beishan area. Low groundwater velocity and dry climatic conditions suggest that dissolution of minerals from the aquifer material controls hydrogeochemical evolution. Water rarely travels from the Beishan area to the Shule valley; therefore, almost all the groundwater in the Shule valley originates from Changma. Global climate change and loss of glaciers in the Qilian Mountains may lead to a reduction of recharge; therefore, the groundwater resources of the Shule valley must be managed to sustain water supply.

Keywords Hydrogeochemistry · Stable isotopes · Groundwater recharge · Arid region · Northwestern China

Introduction

Arid lands, which are found on almost every continent, cover about 40 % of Earth's land surface and feed more than 38 % of the global population (Reynolds et al. 2007); examples of such arid lands can be found in the Midwestern United States, Algeria, Israel, China, and Australia. Common features of arid land include fragile ecological environments, low and irregular precipitation, high temperatures, and high evaporation rates. Because of the scarcity and uncertainty of surface water supply, groundwater is a significant part of the total water resource in arid lands, and plays an important role as water supply for drinking and irrigation (Nativ et al. 1997; Edmunds et al. 2003; Vanderzalm et al. 2011; Keesari et al. 2014). Use of groundwater resources has increased dramatically in the past few years owing to drought, a rapidly growing worldwide economy, and increasing worldwide population. Over-exploitation of groundwater has led to serious consequences, including intense mineralization of groundwater, lowering of the regional water table, desertification, land salinization, degeneration of vegetation, and

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heightened frequency of sand storms (Edmunds et al. 2006; Lapworth et al. 2013). Therefore, it is urgent that limited water resources are used in a sustainable manner, and safeguarding measures must be taken to protect groundwater resources.

Understanding the origin and quality of groundwater is important for sustainable development and effective management of groundwater resources in arid regions (Eissa et al. 2014) However, it is difficult to determine the amounts and sources of groundwater recharge using conventional water balance and/or hydraulics methods. Combined hydrogeochemical and isotopic studies may help elucidate both the sources of groundwater recharge and groundwater hydrogeochemical evolution processes (Bouchaou et al. 2008; Gárfias et al. 2010; Parisi et al. 2011; Diaw et al. 2012). Common methods in this respect include the chloride mass balance method, use of hydrogeochemical tracers (minor or trace metals), and determination of isotopic composition. These techniques can be used to identify sources of groundwater and estimate the contribution of each member (Vanderzalm et al. 2011; Al-Charideh and Hasan 2013; Schulz et al. 2013; Eissa et al. 2014). In arid regions, where there is little precipitation but strong evaporation, hydrogeochemical indicators and stable isotopic groundwater compositions can be effectively employed to trace recharge sources and quantify relative evaporation (Nativ et al. 1997; Vanderzalm et al. 2011; Yangui et al. 2011; Singh et al. 2012; Ahmed et al. 2013; Lapworth et al. 2013). In recent years, new environmental isotope techniques have played an important role in solving the difficult hydrological problems that cannot be solved by conventional methods alone (Negrel et al. 2007; Herczeg and Leaney 2011; Rahobisoa et al. 2014). Several scientists (Edmunds et al. 2006; Ji et al. 2006; Ma et al. 2013; He et al. 2012; Ma et al. 2013) have studied recharge sources and hydrogeochemical evolution of groundwater in many basins (e.g., Minqin, Jinchang, Jiuquan, and Dunhuang) in the Hexi Corridor of northwest China. River waters were considered the main sources of recharge to shallow groundwater, while direct recharge from precipitation was negligible. However, as an important river of the Hexi Corridor, the Shule River was dammed for irrigation in the upstream area near Changma Town (Fig. 1). Groundwater in the Shule valley is being depleted owing to extensive

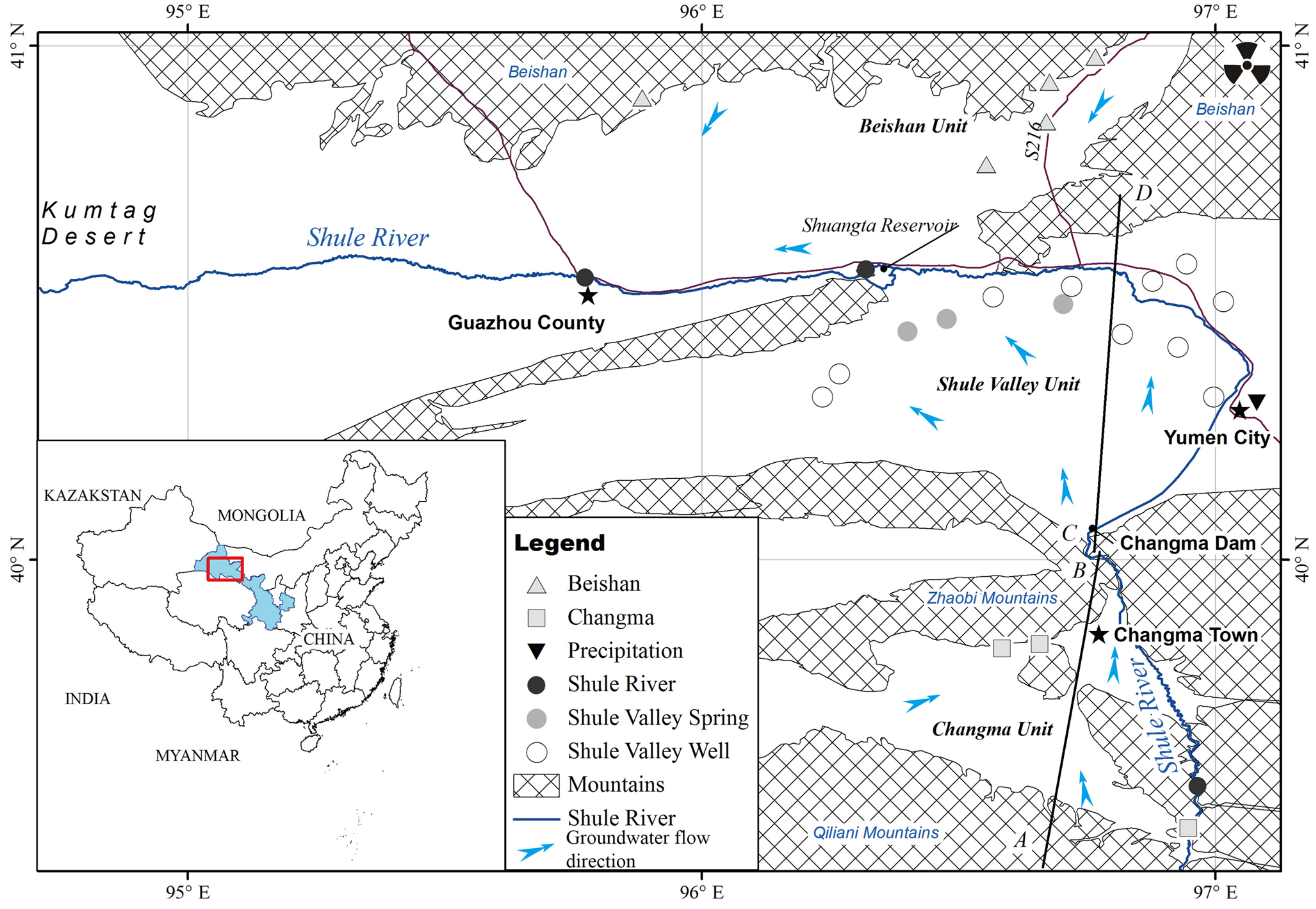

Fig. 1 Location and hydrogeologic features of the study area

extraction versus limited recharge; therefore, it is crucial to understand groundwater recharge, runoff, and discharge in the Shule River basin to maintain the integrity of the flow system.

The Shule River basin, located in the midwestern part of the Hexi Corridor, is an important historic, economic, and ecologic region in China (Ji et al. 2006). Various ancient civilizations, extending back more than 2000 years, were distributed along both sides of the Shule River, associated with features such as the famous ancient Silk Road, the well-known Mogao Caves, and the Great Wall of the Han Dynasty. The Shule River basin is also a conservation area of considerable biological diversity (e.g., Gansu Anxi National Nature Reserve in the hyper-arid desert region) and a major grain producing area of Gansu Province. With more than 550,000 inhabitants, 8.38×10^4 hm^2 of cultivated land, and many factories, water resources are in high demand, especially by agriculture and industry located in the upper–middle reaches of the Shule River (Changma town and Yumen city) (Fig. 1). Because of this demand, water availability is a concern and water resources, groundwater in particular, are threatened. Groundwater in the Beishan area, located about 80 km north of Yumen City, is of great importance because it is a potential area for deep geological disposal of high-level radioactive waste (Guo et al. 2008). Hydraulic connection and potential nuclide migration between the Beishan area and the Shule valley is a significant concern for biosphere security. Analysis of hydrogeochemical and stable isotopic characteristics of groundwater will improve understanding of these systems and their connection.

The objective of this research is to use stable environmental isotopes (^2H or D, and ^{18}O) to determine the sources for groundwater recharge to the upper–middle reaches of the Shule River and adjacent areas, including Changma, the Shule valley, and the southern edge of the Beishan area. In addition, dominant geochemical processes will be characterized using major ions and will help to define possible hydraulic relationships between different sub-basins. Improved understanding of groundwater characteristics and natural evolution can be used when forming scientific guidelines for sustainable use of the region's water resources and help to prevent further degradation of the regional environment.

Study area

Climatic and hydrologic background

The Shule River basin is severely affected by extreme drought because it is located far from the coast, in the interior mainland of China (Fig. 1). The region has low seasonal and annual amounts of precipitation and a relatively high rate of evaporation ($\sim$3,000 mm a^{-1}). The study area is mainly located in the upper–middle reaches of the Shule River. According to geographical and hydrogeological conditions, the study area can be divided into three parts: the Changma unit (i.e., Changma Town), the Shule valley unit (i.e., Yumen City), and the southern edge of the Beishan Mountains (Gansu Geology Survey 1978, Fig. 1). The Changma unit, which lies in the southern part of the study area, is part of a region that includes the Qilian and Altun ranges and covers the upstream reaches of the Shule River. Its elevation ranges from 2,200 to 5,100 m, and it lies within the alpine semiarid climate zone. Annual average temperature and precipitation are in the ranges 0–5.7 °C and 100–320 mm, respectively, within the Changma unit. The Shule valley, which lies within the plains of the Hexi Corridor, is in the center of the study area at an elevation of around 1,200 m. This region is a warm temperate arid zone with an annual average temperature of 8.3 °C, and mean annual precipitation ranging from 37 mm in the west to 62 mm in the east. The Beishan area (or the area along the southern edge of the Beishan Mountains), which lies to the north of the Shule valley, is located within the northern part of the study area at elevations in the range 1,700–2,070 m. This area experiences an average temperature of 6.8 °C and an average annual precipitation of 70 mm.

The Shule River, which is located in the midwestern part of the Hexi Corridor in northwest China's Gansu Province (Fig. 1), originates in the Qilian Mountains at an elevation of around 4,800 m. Most of the river water is impounded by the Changma dam and used for irrigation as part of an inter-basin water allocation program. Some water infiltrates through the gravel of the Changma alluvium to recharge the groundwater, and discharges from springs at the fine soil plain. These springs later converge to form the main stream region of the Shule River. The river flows through the Yumen City and Guazhou–Dunhuang basins from east to west before disappearing at the margins of the Kumtag desert. The Shule River basin has an area of 4.13×10^4 km^2 and a main stream length of 670 km.

Geology and hydrogeology

The Qilian Mountains were uplifted from the end of the Paleozoic through the Mesozoic and created the embryonic form of the Hexi Corridor (Gansu Geology Survey 1978). High-angle reverse faults led to continued subsidence of the Changma basin south of the Zhaobi Mountains, where Quaternary alluvial material accumulated to thicknesses exceeding 200 m during the Middle Pleistocene (Fig. 2). The Shule valley is a vast plain within the Hexi Corridor undergoing intense subsidence as part of the Piedmont

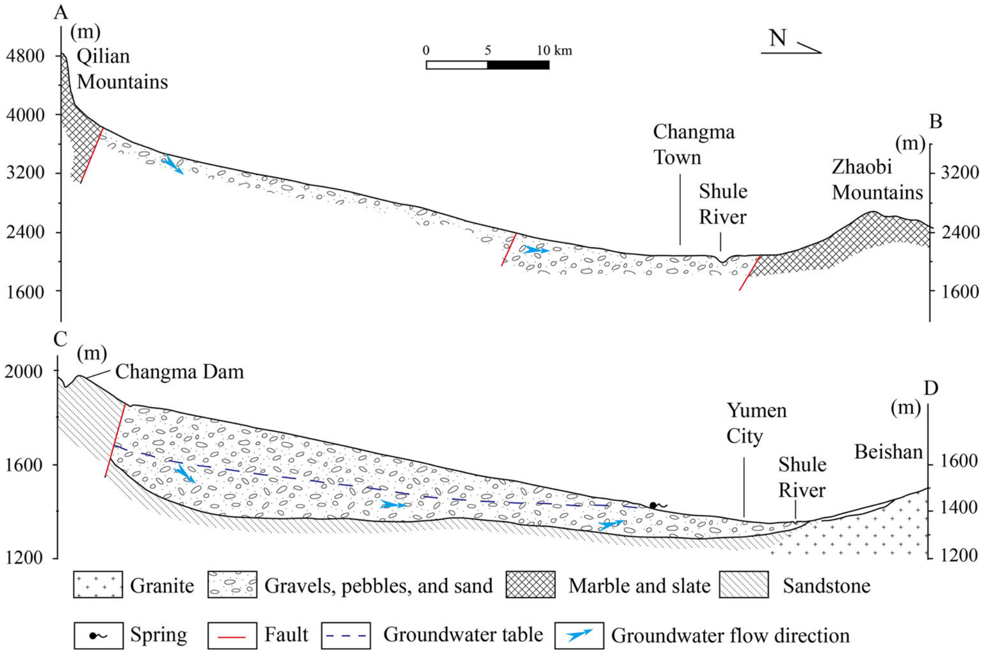

Fig. 2 Hydrogeological cross-sections (*A*–*B*, *C*–*D*, location in Fig. 1) of the study area

subsidence zone. The thickness of the Quaternary sediments ranges from 700 m in the south to 100 m in the north owing to uneven settlement (Fig. 2). The Beishan area is being actively eroded owing to continued uplift; therefore, bedrock (e.g., granite) outcrops and forms hilly terrain.

The Changma unit consists of mountains and inclined piedmont plains. This high-elevation mountainous area is part of the Qilian Mountains and is composed of Archean and Sinian metamorphic and igneous rocks. The low-elevation mountain areas consist of Paleozoic and Mesozoic metamorphic and clastic rocks, and the high-elevation mountainous areas are composed primarily of granite, marble, slate, and quartz-rich sandstone. The strata of the inclined piedmont plains are primarily Quaternary sediments, which are predominantly loose gravel, sand, and loam. Therefore, thick Pleistocene and Holocene diluvial and alluvial sediments constitute the main aquifer in this region. The thickness of the aquifer varies depending on the strata by tens to hundreds of meters. The major aquifer near Changma Town is composed of highly permeable cobble and gravel deposits that are as much as 50–100 m thick. The aquifer system is unconfined, with water levels being between 5 m and 100 m below the surface (Fig. 2). The coefficient of permeability is as high as 20–50 m day^{-1}, and groundwater generally flows from south to north (Fig. 1).

The Shule valley unit comprises the vast plain that lies to the north of Changma and south of Beishan. The valley extends approximately 60 km from north to south, and the strata are primarily Quaternary gravel, sand, and loam. In the center of the valley, the pre-Sinian gneiss and schist occur in ribbon-like outcrops in a very small area extending from Shuangta to south of Guazhou. Groundwater is predominantly stored in the inter-granular pore spaces of gravel and sand. The potentiometric surface is above 100 m at the piedmont, but is close to or above the surface in the fine soil plain of the Yumen region. Salinization of soil is a serious problem in the region because of the shallow groundwater table and excessive irrigation. The primary aquifer changes from a single layer in the south to multiple layers in the north; its coefficient of permeability and specific capacity are 3–35 m day^{-1} and 0.6–3 L s^{-1} m^{-1}, respectively. Groundwater generally flows from south to north; however, in the northern part of the aquifer, groundwater flows from east to west (Fig. 1) to discharge in the Kumtag desert near Dunhuang.

The Beishan unit is mainly composed of granite and granodiorite that formed during the Paleozoic (Caledonian and Hercynian). Owing to a series of complex tectonic events, the rock is cut by fractures and joints are often intruded by diabase. Groundwater is stored in the secondary pore space, which is formed by joints and fractures in the granite. The main aquifer is located in shallow fractured media, and the coefficient of permeability and specific capacity are approximately 0.1–1.3 m day^{-1} and 0.01–0.1 L s^{-1} m^{-1}, respectively. Consistent with the topography, groundwater flows from north to south.

Materials and methods

A total of 25 specimens were collected from August to November in 2012, including one precipitation specimen collected in Yumen City, three spring specimens in

Changma, ten groundwater well specimens and three spring specimens in the Shule valley, three river specimens from the Shule River, and five spring specimens from Beishan (Table 1).

A sample of snow was collected in Yumen City, Shule valley, on November 21, 2012, and used to represent the Shule valley's precipitation. The sample was collected in a plastic bag, sealed, allowed to melt, and then poured into a pre-cleaned polyethylene bottle. Spring samples were collected at the outcrops to be representative of in situ conditions. Well water was collected from water supply and irrigation boreholes that penetrated multiple aquifers and were continuously pumping for at least 1 month prior to sampling. All samples were stored below 4 °C prior to analysis. Temperature, pH, and total dissolved solids (TDS) were measured onsite using a SensION156 portable multi-parameter meter (Hach, Loveland, CO). Total alkalinity (HCO_3^-) was determined at the time of sampling by titration to a fixed end-point pH. Five bottles of each sample (a total of 1.5 L per sample) were filtered through a membrane filter (0.45 μm), and then transferred to five pre-cleaned polyethylene bottles. Samples were acidified in two of the five bottles using ultra-pure HNO_3 (99.999 %) so that a resulting pH $\leq$ 1.5 would stabilize trace metals. Water samples from the other three bottles were not acidified because they were analyzed for anions and stable isotopes.

Cations and anions were analyzed at the Key Laboratory of Engineering Geomechanics, Institute of Geology and Geophysics, Chinese Academy of Sciences (CAS). Concentrations of major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), above a detection limit of 0.01 mg/L, were measured by inductively coupled plasma mass spectrometry (ICP–MS, Agilent Technologies, CA). The accuracy of ICP–MS analyses was controlled using appropriate laboratory standards and checked during each batch using international reference standards. Concentrations of major anions (SO_4^{2-}, Cl^-, and NO_3^-) above a detection limit of 0.01 mg/L were measured by ion chromatography (IC). Concentrations of cations and anions were validated using the ionic balance method, and all samples had a precision better than 5 % (Table 1).

Stable isotopic composition was analyzed using a DLT-100 liquid water isotope analyzer (Los Gatos Research, Inc., Mountain View, CA) at the Key Laboratory of Water Cycle and Related Land Surface Processes, Institute of Geographic Sciences and Natural Resources Research, CAS. The stable isotopic compositions (^{2}H or D, and ^{18}O) are reported in standard δ notation in units of per mil (Table 1) relative to Vienna Standard Mean Ocean Water (VSMOW). The isotopic composition of each sample was measured five times to ensure reliability. Based on these measurements, the analytical reproducibility was 1 ‰ for δD and 0.1 ‰ for δ^{18}O. PHREEQC (Parkhurst and Appelo 1999) was employed to calculate mineral saturation indices in equilibrium with groundwater, and the results are shown in Table 2.

Results

Stable isotope distributions

Isotopic and geochemical results (including type information or well depth, stable isotope concentrations, field data, and major ions, among others) for rainwater, river water, and groundwater are shown in Table 1. Sampling sites are shown according to sample type (Fig. 1); it should be noted that GZ01 is rainwater, and GZ02, GZ03, and GZ04 were taken in the upstream, midstream, and downstream portions, respectively, of the Shule River. All other samples are groundwater and are arranged in Table 1 according to their geological and hydrogeological conditions, separated into the Changma unit (GZ05–07), the Shule valley unit (spring samples GZ08–10, 12, 13; well samples GZ11–20), and the Beishan area (GZ21–25).

The δD and δ^{18}O values of rainwater from Yumen City are −144 and −19.0 ‰, respectively, indicating significant depletions in heavy isotopes. These values coincide with the global meteoric water line (GMWL) of $\delta D = 8.0\ \delta^{18}O + 10.0$ (Craig 1961), which is representative of modern precipitation. In contrast, δD and δ^{18}O compositions range from −61 to −56 ‰ and −9.5 to −8.5 ‰ for the Shule River, indicating that they are significantly depleted in heavy isotopes relative to precipitation.

The δD and δ^{18}O values of spring samples, collected in the Changma unit, range from −78 to −66 ‰ (−74.14 ‰ on average) and from −12.1 to −10.4 ‰ (−12.12 ‰ on average), respectively, with a good linear relationship between δD and δ^{18}O values. Groundwater specimens from the Shule valley have δD and δ^{18}O values of −64 to −58 ‰ and −10.5 to −8.6 ‰, respectively, indicating that they are slightly enriched in heavy stable isotopes relative to those from the Changma region.

Previous studies have found that groundwater samples from the Beishan region plotted on both sides of the GMWL, although most plotted below the GMWL (e.g., Guo et al. 2008). In the present study, the δD of springs ranged from −83.4 to −64.16 ‰, with a mean value of −72.13 ‰, whereas δ^{18}O ranged from −11.2 to −8 ‰, with a mean of −9.57 ‰.

Hydrogeochemistry of groundwater

The precipitation collected from Yumen City is alkaline (GZ01, pH = 8.2,) and has a low TDS value (46.4 mg/L)

Table 1 Basic physical and chemical data for groundwater and surface water in the study area

Sample ID	Type or Well depth (m)	δD (‰)	$\delta^{18}O$ (‰)	Temp. C	pH	TDS (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- N (mg/L)	Hardness (mg/L)	Br (μg/L)
GZ01	Precipitation	−144	−19	–	8.2	46.4	2.07	1.23	0.61	11.7	2.19	54.9	6	0.66	31.8	3.17
GZ02	Shule River surface water	−61	−9.5	0.3	7.5	417	37.4	2.22	36.3	66.7	61.35	242	144	0.79	318	27.1
GZ03		−56	−8.5	4.4	8.14	435	48.8	3.72	41.5	51.5	62.52	192.2	184.25	0.4	301.7	29.8
GZ04		−56	−9.1	1.8	8.22	495	76.9	4.08	50.3	56	84.8	208.7	232.96	0.55	349.6	35.7
GZ05	Changma spring	−78	−11.9	3.7	7.88	281	17.9	2.07	30.7	38.7	29.37	208.7	74.6	1.31	224.7	12.5
GZ06		−78	−12.1	5.7	7.91	243	12.4	1.42	28.5	35.8	14.36	221.6	47.47	0.61	208.3	9.45
GZ07		−66	−10.4	7.5	8.09	235	9.58	1.72	28.7	40.3	9.96	194.2	90.58	0.78	220.3	7.89
GZ08	Shule valley spring	−59	−9.5	9.1	7.66	484	57.07	5.4	59.1	45	88.9	232.01	192.11	0.34	347	83.7
GZ09		−61	−9.9	12.6	8.25	290	32.6	2.49	29.7	30.6	43.28	175.7	91.95	0.99	200.3	26.1
GZ10		−61	−9.9	11.5	8.11	472	48.3	2.88	46.6	50.7	86.04	164.8	177.99	0.8	320.9	37.3
GZ11	90	−64	−10.5	9.6	8.05	384	41.2	2.56	44.1	43.3	47.01	223.6	132.94	1.89	292	30.8
GZ12	90	−61	−10	11.6	7.76	298	28.6	2.24	31.6	34.2	39.55	197.7	89.41	0.84	217.2	21.5
GZ13	80	−59	−9.4	10.1	8.04	474	54.2	5.2	53.9	41.1	77.48	225.2	185.52	0.65	327.3	33.5
GZ14	95	−58	−8.7	10.4	7.47	498	65.25	4.09	70.59	71.49	69.58	405.02	132.06	3.88	–	31.98
GZ15	80	−60	−8.6	11.1	7.53	503.5	63.86	3.74	55.08	53.41	62.59	361.2	74.43	3.52	–	33.51
GZ16	80	−65	−9.9	10.5	7.56	452	58.66	3.68	38.39	47.65	54.93	328.49	71.06	1.26	–	25.74
GZ17	100	−64	−9.8	10.8	7.63	411	54.24	3.12	39.18	42.22	63.91	264.08	64.05	1.31	–	22.37
GZ18	95	−58	−9.1	10.7	7.34	555	57.74	3.54	58.44	63.86	62.39	414.94	80.6	4.11	–	31.83
GZ19	95	−63	−9	8.6	7.55	397	31.11	3.87	50.69	45.84	36.59	397.14	45.99	<0.03	–	29.92
GZ20	100	−64	−9.6	11.5	7.74	353	37.47	2.25	43.74	38.2	50.02	311.2	55.64	<0.03	–	37.04
GZ21	Beishan spring	−70	−9.5	7.8	6.97	4,050	823	14.4	39.6	278	977.5	223.2	1,305.88	<0.03	860	88.3
GZ22		−75	−10.7	8.9	7.45	1,339	326	7.96	8.71	118.5	405	120.8	434.73	1.28	256.3	45.1
GZ23		−60	−8.6	12.1	7.66	783	192	3.4	11.3	57.9	220.62	149.3	229.92	4.44	191.8	57
GZ24		−64	−8.9	6.7	7.57	1,862	495	8.96	23.7	153.2	524.24	153.8	748.27	7.06	348.8	70.6
GZ25		−80	−9.2	7.9	6.96	3,980	857	8.1	5.19	352	992.61	29	1,537.76	1.29	901.6	130.7

Table 2 Saturation indices for commonly occurring minerals

Sample no.	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum	Halite
GZ01	−3.53	−0.80	−0.64	−2.65	−3.28	−9.81
GZ02	−2.18	−0.10	0.06	0.02	−1.93	−7.80
GZ03	−2.40	−0.03	0.13	0.21	−2.14	−8.27
GZ04	−2.09	0.16	0.32	0.56	−1.84	−8.65
GZ05	−1.97	0.20	0.36	0.84	−1.72	−7.26
GZ06	−2.19	−0.17	−0.02	0.09	−1.94	−7.49
GZ07	−1.89	0.15	0.31	0.87	−1.64	−6.94
GZ08	−1.85	0.08	0.23	0.59	−1.6	−6.91
GZ09	−2.17	−0.01	0.15	0.44	−1.91	−6.96
GZ10	−2.2	−0.05	0.11	0.25	−1.94	−7.05
GZ11	−2.28	−0.11	0.05	0.2	−2.02	−7.01
GZ12	−2.08	−0.06	0.09	0.28	−1.82	−7.01
GZ13	−0.03	2.44	2.59	5.1	0.22	−4.85
GZ14	−0.01	2.49	2.65	5.3	0.23	−4.64
GZ15	−1.83	−0.27	−0.11	−0.10	−1.57	−6.84
GZ16	−2.23	0.23	0.38	0.92	−1.97	−7.40
GZ17	−1.81	0.21	0.36	0.85	−1.56	−6.94
GZ18	−1.72	−0.28	−0.12	−0.58	−1.47	−7.17
GZ19	−1.76	0.20	0.36	0.64	−1.50	−7.06
GZ20	−1.65	0.28	0.44	0.79	−1.39	−6.73
GZ21	−0.61	−0.43	−0.27	−1.40	−0.35	−4.73
GZ22	−1.32	−0.49	−0.33	−1.55	−1.06	−5.47
GZ23	−1.67	−0.24	−0.08	−0.71	−1.41	−5.95
GZ24	−1.13	−0.32	−0.16	−0.88	−0.88	−5.19
GZ25	−0.49	−1.21	−1.05	−3.83	−0.23	−4.72

Values were calculated using the PHREEQC software for groundwater in the study area

(Table 1), with concentrations of major ions (e.g., Na^+, K^+, Mg^{2+}, Cl^-, and SO_4^{2-}) typically less than 10 mg/L. Hydrochemical analyses indicate that the sum of HCO_3^- and Ca^{2+} in precipitation is greater than 80 % (milligram equivalent) of the total alkalinity, suggesting that precipitation is predominantly of HCO_3^-–Ca^{2+} type (Fig. 3).

The TDS values of surface water vary from 417 mg/L (GZ02) in the upstream reaches to 435 mg/L (GZ03) in the Shuangta reservoir, and 495 mg/L (GZ04) in the downstream reaches near Guazhou County. The temperature is low and was approximately the same as the air temperature at the time of sampling. The surface water hydrogeochemical content was not dominated by specific anions or cations; thus, all the samples were plotted in the center of a trilinear (e.g., Piper) diagram (Fig. 3). Concentrations of Mg^{2+} and SO_4^{2-} in surface water samples clearly increase downstream, whereas those of Ca^{2+} and HCO_3^- decrease downstream.

The spring samples from the Changma unit are characterized by low temperature (5 °C), low pH (~8), and low TDS values (mean of 253 mg/L). Magnesium and calcium, the most abundant cations, vary between 28.5 and 30.7 mg/L and between 35.8 and 40.3 mg/L, respectively. Bicarbonate is the predominant anion, ranging from 194.2 to 221.6 mg/L; therefore, the groundwater in Changma is of Mg^{2+}–HCO_3^- and Ca^{2+}–HCO_3^- type (Fig. 3).

In the Shule valley, groundwater samples were collected from springs and wells; however, hydrogeochemical analyses demonstrated little difference between these two sample types. All of the samples plot within a narrow temperature range (9.1–12.6 °C), with similar pH values (~7.8) and a narrow range of TDS values (290–555 mg/L, with a mean value of 432.4 mg/L). In the case of the Shule valley groundwater, the contents of Na^+ and Cl^- and the TDS value are slightly higher than those of the groundwater samples from the Changma area (Table 1). Groundwater from the Shule valley is predominantly of Mg^{2+}–HCO_3^- type or Mg^{2+}–HCO_3^-–SO_4^{2-} type (Fig. 3).

Samples collected in the Beishan area were spring water, with temperature of about 8.7 °C, pH lower than 7.7, and TDS values ranging from 738 to 4,050 mg/L (mean of 2,008.5 mg/L); these are much higher than the TDS values of other units. Chloride (620 mg/L) and sulfate (851 mg/L) are the most abundant anions, and sodium is the most abundant cation, whose values vary between 192 and 857 mg/L. Therefore, most of the groundwater samples from the Beishan are of Na^+–Cl^-–SO_4^{2-} type (Fig. 3).

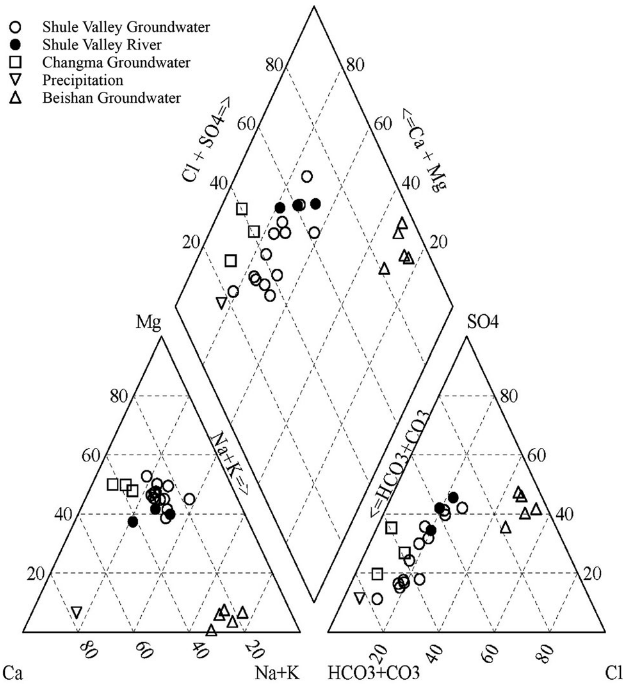

Fig. 3 Trilinear diagrams illustrating the chemical composition of surface water and groundwater in the study area

Discussion

Based on the hydrogeological background and hydrogeochemical data, the study area can be divided into two parts: Changma and the Shule valley (C–S), and the Beishan area (B–A).

Groundwater origin

Generally speaking, precipitation is an important source of water for recharging groundwater systems. The H and O stable isotope concentrations of samples differ from those of precipitation, indicating varying amounts of isotope fractionation during the evaporation and condensation process. Several factors, including latitude, elevation, temperature, and precipitation amount, can lead to noticeable changes in hydrogen and oxygen isotope compositions. In the study area, there is a notable elevation effect (e.g., mountains versus plains) on precipitation, such that the linear correlation between δD and $\delta^{18}O$ is a function of elevation. As a result, the source and circulation history of groundwater can be deciphered by comparing the stable isotopes (^{2}H or D, and ^{18}O) of precipitation and groundwater.

The Zhangye meteorological station (100°28′ E, 38°55′ N, 1,485 m), set by the International Atomic Energy Agency (IAEA), is close to the sampling locations (350 km southeast of the study area). It can provide daily precipitation (mm), air temperature (°C) and stable isotope concentrations (δD and $\delta^{18}O$) from 1985 to 2003. The local meteoric water line (LMWL) at the Zhangye station is $\delta D = 7.5\delta^{18}O + 2.7$ (IAEA and WMO 2006), and both the slope and intercept of this line are lower than those of the GWML. These differences indicate that water vapor formed from rainfall was depleted in heavy isotopes owing to evaporation processes. This phenomenon has been found in many arid regions worldwide and reported extensively (e.g., Gat 1980). The isotopic values of precipitation at Yumen City are −144 ‰ δD and −19.0 ‰ $\delta^{18}O$ (Table 1, Sample ID: GZ01), indicating depletion in heavy isotopes. Only a single precipitation sample, collected in winter, plots on the GMWL rather than the Zhangye LMWL, likely because the isotopic values of precipitation exhibit considerable seasonal variation. Long-term data from the Zhangye station were selected as representative of precipitation in the plain zone. The Yeniugou station, which was not set by the IAEA, is located in the Qilian Mountains (99°38′ E, 38°42′ N, 3,320 m) and is approximately 300 km southeast of the study area. More than 1 year of data provided by Zhao et al. (2011) include daily precipitation (mm), air temperature (°C), relative humidity (%), and stable isotope concentrations (δD and $\delta^{18}O$). The LMWL of the Yeniugou station follows the equation of $\delta D = 7.6\delta^{18}O + 12.4$ ($R^2 = 0.989$, $n = 99$), with a slope of 7.65, indicating that more moisture and less evaporation can be found at high elevations (i.e., in the mountains). Thus, this station can be considered representative of precipitation at high elevations in the Qilian Mountains.

The δD and $\delta^{18}O$ values of groundwater from Changma plot close to the Yeniugou LMWL (Fig. 4), indicating that the precipitation in the Qilian Mountains is the primary source of groundwater in the Changma region. Wells are rare in Changma because the abundant surface water resources are sufficient for use; therefore, only three groundwater samples were collected (from springs) in Changma. The weighted average isotopic values (−74.14 ‰ δD and −12.12 ‰ $\delta^{18}O$) of these three samples were approximately the same as the weighted average isotopic values (−120.9 ‰ δD and −18.1 ‰ $\delta^{18}O$ in 2008, −82 ‰ δD and −12.8 ‰ $\delta^{18}O$ in 2009) of winter precipitation at Yeniugou. This indicates that the main recharge source is winter precipitation in the Qilian Mountains.

Most of the groundwater samples in the Shule valley are distributed near the Yeniugou LMWL, but are more enriched with heavy isotopes compared to the Changma samples (Fig. 4). This indicates that the groundwater in the Shule valley is also sourced from precipitation in the Qilian Mountains and has undergone intensive evaporation. In addition, three groundwater samples (GZ14, GZ19, and GZ20) deviate slightly from the Yeniugou LMWL, possibly owing to greater runoff distance and more evaporation. Groundwater and surface water stable isotopic

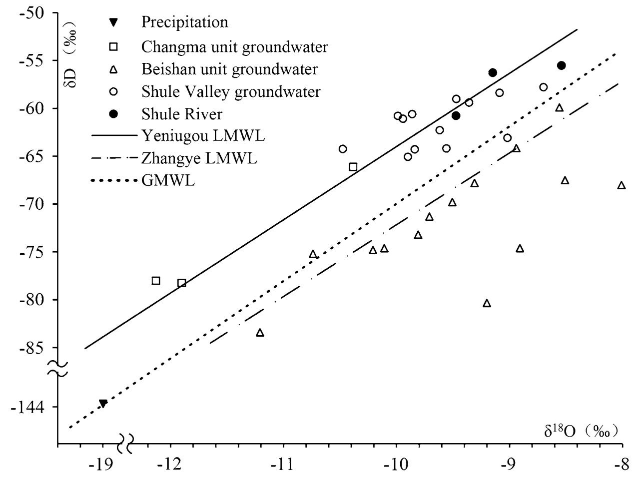

Fig. 4 A plot of δD and δ^{18}O for groundwater and surface water in the study area (some data for Beishan are from Guo et al. 2008)

compositions overlap in Fig. 4, indicating that the groundwater and surface water systems are closely connected. This is evident in the upstream region of the Shule River, where surface water seeps easily through the riverbed and recharges groundwater. Conversely, groundwater discharges from the aquifer into the Shule River in the fine soil plain.

The weighted mean values of δD and δ^{18}O at Zhangye have been shown to be −43.2 and −6.3 ‰, respectively (IAEA and WMO 2006). Compared with these values, all of the groundwater samples in the Shule valley are strongly depleted, indicating that local precipitation is not a primary source of groundwater recharge in the plain region. In addition, Edmunds et al. (2006) used the Cl^- mass balance method to calculate an average direct local rainwater recharge rate of around 0.95–3 mm/yr in the nearby Minqin basin, which has an annual rainfall of 89–120 mm. The Minqin and Shule basins have similar geographical and hydrogeological conditions; therefore, it is assumed that direct recharge of the groundwater aquifers by rainfall in the study area is much less than 1 mm/year. Similar findings have been reported in adjacent areas, for example, in the Jinchang, Dunhuang, and Jiuquan basins (Ma et al. 2010; He et al. 2012; Ma et al. 2013).

Deuterium excess (d-excess) values were defined by Dansgaard (1964) as follows: $d = \delta D - 8\ \delta^{18}O$. These values can help gain additional insight into the evolution of groundwater salinity. Fundamentally, the *d*-excess value is simply another index that describes the effect of evaporation on the physicochemical characteristics of water, and the *d*-excess value will decrease when water evaporates. The mean *d*-excess values of groundwater in Changma and the Shule valley are 17.7 and 14.9, respectively, indicating that more intensive evaporation has occurred in the Shule valley than in Changma. This is consistent with hydrogeological conditions: that is, groundwater in Changma recharges into the aquifer of the Shule valley by lateral runoff and undergoes evaporation during this process owing to the dry climate.

Most groundwater samples in the Beishan area plot along the Zhangye LMWL (Fig. 4) and have a relatively low d-excess value (4.4 ‰), which is similar to that obtained from the Zhangye station (6.8 ‰). This indicates that water vapor in Beishan has undergone secondary evaporation under dry climate conditions, similarly to the processes that were found at Zhangye. Depletion of heavy isotopes in the Beishan groundwater samples indicates that precipitation is the major source of groundwater recharge. One exception was found for the sample BS19, which is enriched with the heavy oxygen isotope, with a maximum offset of approximately 2 ‰. This may be due to long-term water–rock interaction between the groundwater and the surrounding granite owing to the low groundwater velocity.

In summary, there are two sources of groundwater in the study area. Similarities in isotopic characteristics between the groundwater of C–S and precipitation in Yeniugou indicate that the groundwater in these two areas was likely sourced primarily from precipitation over the Qilian Mountains. The groundwater of the Beishan area also is recharged by local precipitation, although secondary evaporation that occurs during precipitation can lead to depletion of the heavy isotope.

Evolution of groundwater hydrochemistry in different units

Generally, groundwater or surface water samples have low alkalinity, with two exceptions (GZ21 and GZ25, Fig. 5a) collected from the Beishan area. GZ21 and GZ25 have pH values that are approximately equal to 7, which is lower than the mean pH value of Beishan area groundwater (7.32). In addition, groundwater salinity increases gradually from the Changma unit to the Shule valley unit (Fig. 5b), and the most abundant anions change from HCO_3^- and SO_4^{2-} to Cl^- (Fig. 3). This is consistent with the evolutionary trend of groundwater from recharge area to discharge area in arid regions (Nativ et al. 1997).

Generally, bromine and chlorine in water undergo few chemical and biological reactions in a natural environment; thus, the Br^-/Cl^- ratio can be used as a reference to understand the evolution of other ions and the salinity of groundwater, especially in arid areas. Many studies of the Br^-/Cl^- ratio of water suggest that it may be used as an indicator of the origin of salinity (Edmunds 1996; Cartwright et al. 2006). In this study, the Br^-/Cl^- ratio of precipitation from Yumen City is 0.0015, which is typical of inland precipitation and depleted relative to sea water

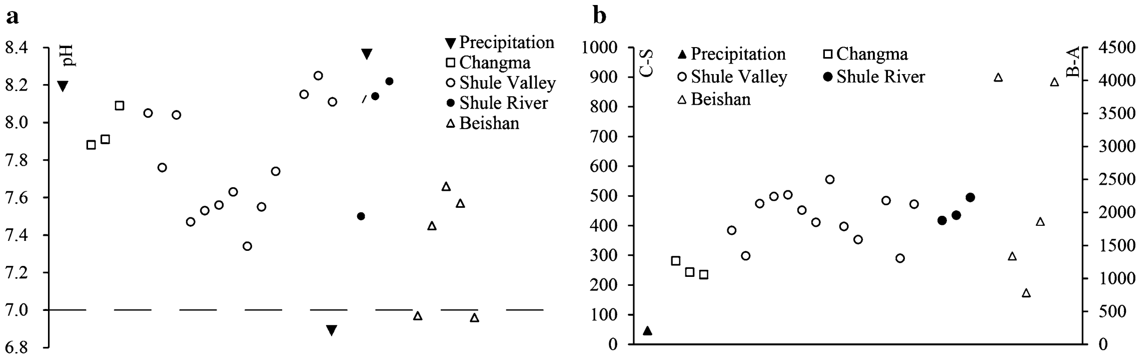

Fig. 5 Distribution of pH and TDS in water samples

(0.0035) (Davis et al. 1998). The Br^-/Cl^- ratio in precipitation commonly behaves conservatively during transit through regional aquifers. Because Br^- is rejected during the process of halite precipitation, the Br^-/Cl^- ratio of solid halite is usually 2–3 orders of magnitude lower than that of the original waters. The Br^-/Cl^- ratio that would result from dissolution of halite will be low because of the low Br^- content of halite (Edmunds 1996). The average values of groundwater Br^-/Cl^- ratio in C–S and B–A are 0.00059 and 0.00015, respectively. This may indicate that Cl^- mainly originates from the dissolution of halite in evaporite deposits or originates partly by evaporative enrichment from precipitation. Thus, Cl^- content increases when groundwater flows over long distances in arid lands, and the Cl^- content in the Shule valley (mean value 60.18 mg/L) is higher than that of Changma (mean value 17.89 mg/L) owing to the longer flowpaths.

Statistical analysis of the dissolved species in groundwater can be used to study the characteristics and mineralization sources of the groundwater. In the present study, Cl^-concentrations correlate with TDS for C–S (Fig. 6a: $R^2 = 0.94$), suggesting that TDS increases continuously along the groundwater flow path. Other major ions, for example SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}, also exhibit linear correlation with TDS, indicating that minerals dissolved into groundwater contribute most of the salinity to the groundwater. In addition, a linear relationship was found between Na^+ and Cl^- for the groundwater samples from C–S. The mNa^+/Cl^- ratio (molar) is stable, with a linear relationship of $Na^+ = 1.08Cl^- + 0.23$ (Fig. 6b; $R^2 = 0.76$). Since the unsaturated zone in this area is extremely thick, evaporation from groundwater is assumed to be negligible; therefore, dissolution of halite is assumed to be a significant factor controlling Na^+ and Cl^- concentrations. Abundant halite can dissolve continuously in the groundwater because the saturation indices of all samples for C–S are much lower than 0 (Table 2). Although K^+ and Cl^- are also correlated ($R^2 = 0.77$), the mK^+/Cl^- ratio is 0.04, which indicates that K^+ is derived from dissolution of sylvite but is negligible with respect to other sources.

The mMg^{2+}/Na^+ ratio ranges from 1.25 to 7.26 (Fig. 6c), with most values being greater than 1.8. The mean value of the mMg^{2+}/Ca^{2+} ratio is greater than 1.6, which is consistent with the abundant Mg-rich lithology of C–S. In addition, the plot of Mg^{2+}+Ca^{2+} versus $SO_4^{2-} + HCO_3^-$ (Fig. 6d, $R^2 = 0.95$) indicates that the Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- ions are derived from dissolution of calcite, dolomite, and gypsum. Most of the samples collected from C–S are close to or slightly above saturation with respect to aragonite, calcite, and dolomite (Table 2). Meanwhile, the results also suggest that dissolution is a major hydrogeochemical process in this region.

Groundwater from C–S exhibits low NO_3^- and hardness, with mean concentrations of 1.39 and 260 mg/L, respectively. These concentrations are substantially lower than the acceptable levels provided by the World Health Organization (2011); therefore, groundwater in the arid area is of sufficient quality for drinking and irrigation.

The Cl^-, SO_4^{2-}, HCO_3^-, Na^+, and Ca^{2+} concentrations in B–A are correlated with TDS. In addition, Na^+ and Cl^- are strongly correlated for B–A according to the relationship $Na^+ = 1.31Cl^- + 0.3919$ (Fig. 7a $R^2 = 0.99$). The mNa/Cl molar ratio is greater than one for all samples in B-A, indicating that excess Na is a result of mineral dissolution. The mMg^{2+}/Na^+ values in B–A are between 0.01 and 1.53 (Fig. 7b) and the mean value of mMg^{2+}/Na^+ is 0.4, suggesting that excess Na could be provided by the Na_2SO_4 that has been identified at Glauber's salt mines in B–A. The Na^+ and SO_4^{2-} ions exhibit a strong linear correlation ($R^2 = 0.99$) and the molar ratio (0.90) is very close to one. Furthermore, there is also a good correlation between Mg^{2+}+Ca^{2+} and $SO_4^{2-} + HCO_3^-$ (Fig. 7c, $R^2 = 0.96$), but the slope is only 0.58. This indicates that the Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- ions may be derived from not only dissolution of calcite, dolomite, and gypsum, but also from other reactions.

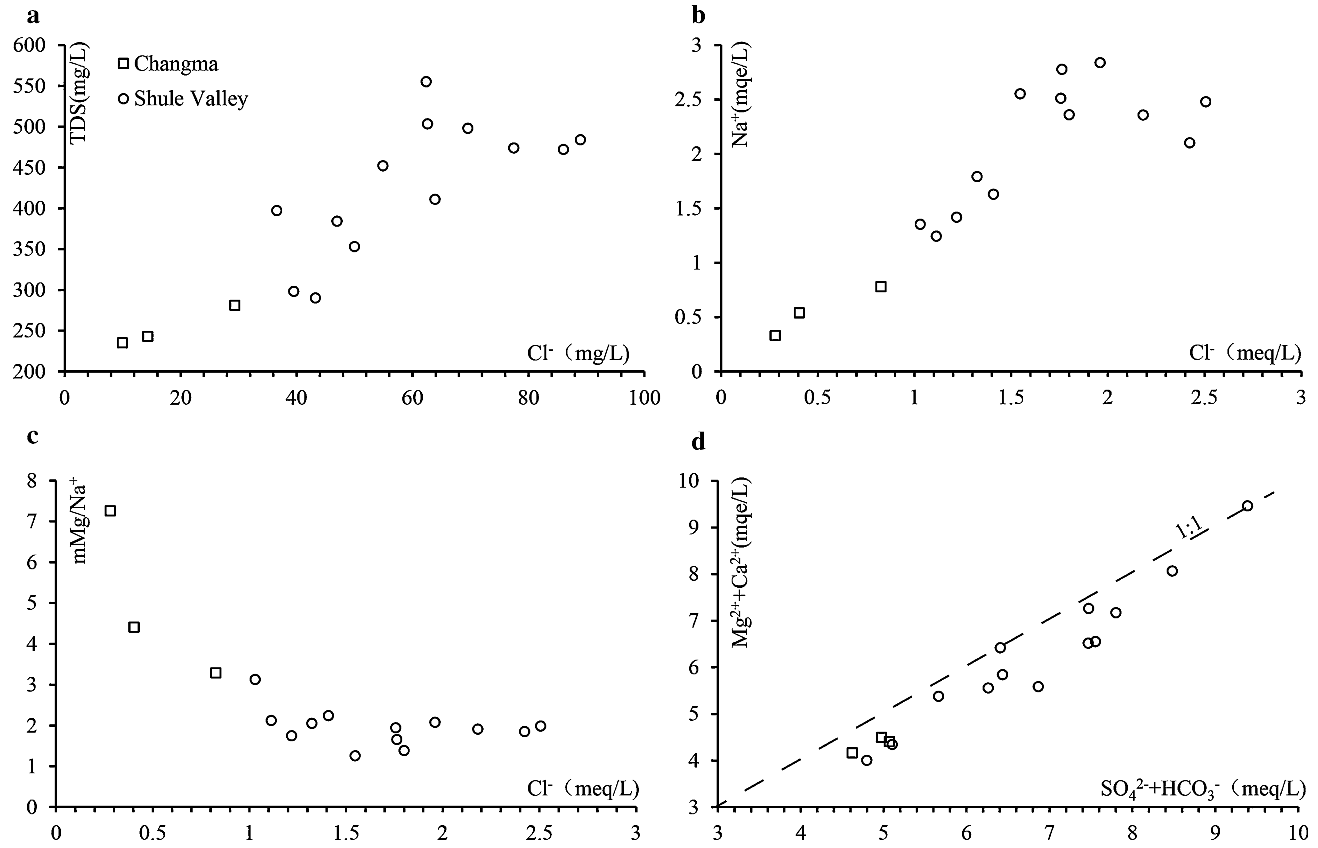

Fig. 6 Relationships between various ions in groundwater for C–S

In addition to the dissolution and concentration processes, ion-exchange reactions can also play a role in determining groundwater compositions. Schoeller (1965) defined two chloroalkaline indices, as follows:

$$\begin{cases} \text{CAI 1} = \text{Cl}^- - [(\text{Na}^+ + \text{K}^+)/\text{Cl}^-] \\ \text{CAI 2} = \text{Cl}^- - \left[(\text{Na}^+ + \text{K}^+)/\text{SO}_4^{2-}\right] + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^- \end{cases}$$

Both CAI 1 and CAI 2 are positive when ion exchange occurs between Na^+ in the groundwater and Ca^{2+} or Mg^{2+} in aquifer materials. This phenomenon occurs markedly in B–A (Fig. 7d) because CAI 1 ranges from 4.86 to 26.62 and CAI 2 ranges from 6.97 to 29.87. This indicates that cation exchange of sodium with calcium or magnesium is likely to occur in B-A. However, despite all CAI 2 values being positive, the CAI 1 values of most of samples from C–S are less than zero. This suggests that ion-exchange reactions in C–S are weaker than those in B-A.

Because coarse gravels and pebbles are deposited on top of the Changma alluvial fan, precipitation and meltwater can quickly seep into the aquifer without significant evaporation. In addition, the percolation of groundwater likely proceeded rapidly owing to the steep hydraulic gradient and enhanced permeability of the alluvial fan. Therefore, the low TDS groundwater of Changma can flow quickly through the aquifer and enter the Shule valley. Dissolution is the major hydrogeochemical process that occurs along the groundwater flow path, with minerals present in the aquifer media dissolving continuously into the groundwater. As a result, the TDS of the Shule valley groundwater is higher than that of the Changma groundwater; however, groundwater in both of these regions is potable owing to the relatively low salinity. In stark contrast to C–S, the mean TDS values of B–A are greater than 1 g/L. The most abundant ions in groundwater samples from B–A are Na^+, Cl^-, and SO_4^{2-}; this composition is distinctive, typically found for groundwater in arid regions, and is an indicator that concentration is the dominant hydrogeochemical process in B–A.

Hydrogeologic conceptual model

Based on the isotopic and hydrogeochemical analysis, a conceptual model of groundwater flow patterns was developed to help understand groundwater evolution in the study area. This model is described in detail here.

The relatively abundant precipitation (~300 mm a^{-1}) in the Qinlian Mountains and high permeability of the

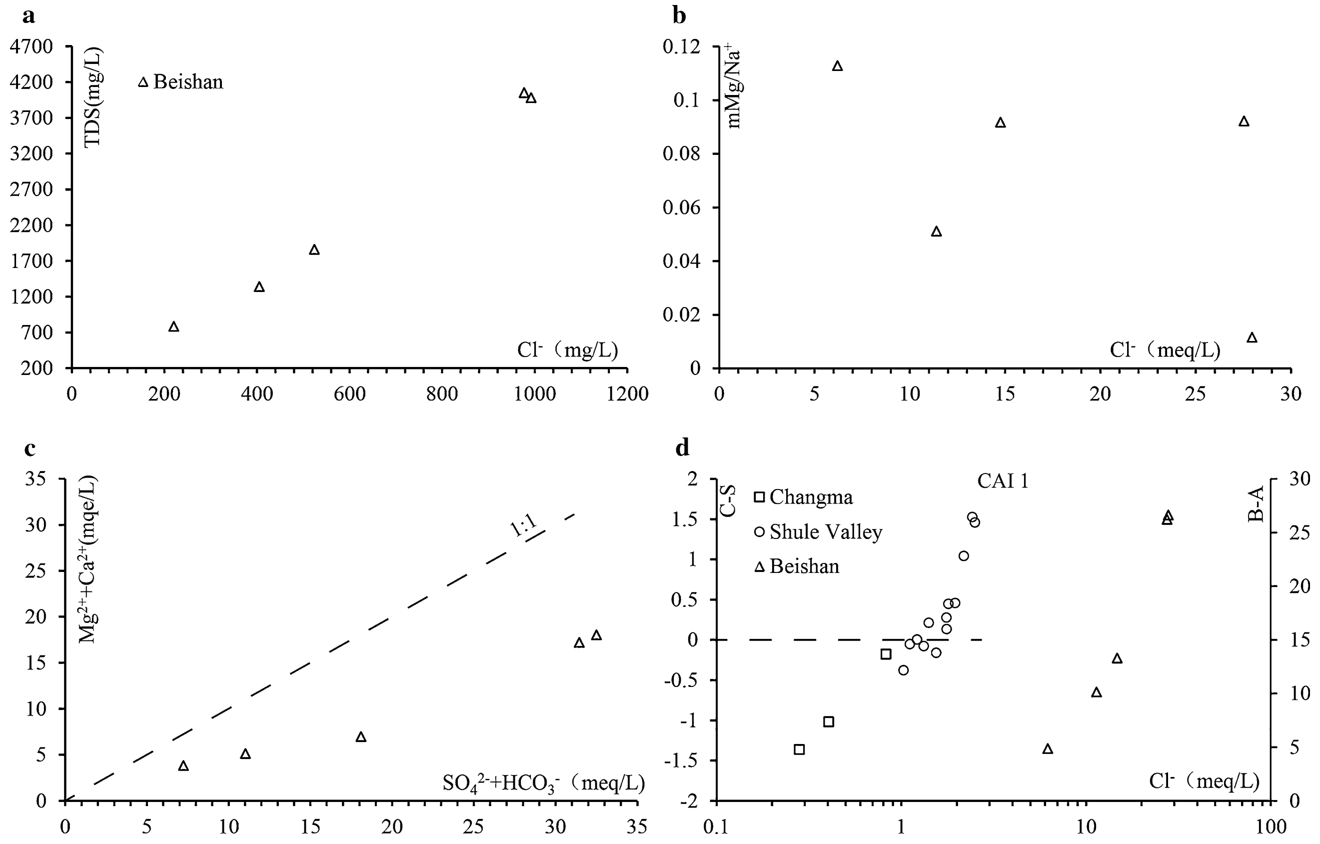

Fig. 7 Relationships between various ions in groundwater for B–A

vadose zone allow precipitation and meltwater to infiltrate into the aquifer easily and comprise the main source of groundwater recharge in Changma. The groundwater flows from south to north through Changma and enters the aquifer of the Shule valley. During this process, aquifer material is dissolved into the groundwater with low TDS. A weaker cation exchange reaction occurs in C–S owing to the rapid groundwater flow; therefore, dissolution is likely the dominant process affecting the hydrogeochemical evolution of groundwater. The hydraulic connection between Changma and the Shule valley allows lateral flow from Changma to act as the primary source of groundwater recharge, whereas input from local precipitation is negligible.

Local precipitation is the primary source of recharge in the Beishan area. However, because the climate is very dry and the permeability of the aquifer is extremely low, only a small fraction of the precipitation that falls ends up recharging groundwater. Long-term water–rock interactions lead to high concentrations of dissolved ions in groundwater. Furthermore, although the groundwater flows primarily from north to south, only a small amount of lateral flow occurs from Beishan to the Shule valley, owing to the low permeability of the Beishan aquifer (Fig. 8).

Conclusions

Hydrogeochemical and isotopic methods were employed to understand the recharge sources and geochemical evolution of groundwater in the upper–middle reaches of the Shule basin and adjacent areas midwest of the Hexi Corridor, including Changma, the Shule valley, and the Beishan area. Infiltration of rainwater and meltwater in the Qilian Mountains are major sources of recharge for groundwater in Changma. The groundwater in the Shule valley is supplied by lateral flow from Changma, whereas direct infiltration of local precipitation is negligible, despite an average of 60 mm of annual precipitation in the Shule valley. This is similar to the neighboring Jiuquan basin and Shiyang River basin (He et al. 2012; Edmunds et al. 2006). In contrast, local precipitation is the primary source of recharge for groundwater in the Beishan area. The stable isotopic signature of groundwater from C–S is distinct from that of B–A. In particular, the isotopic values of groundwater from C–S are distributed along the Yeniugou LMWL and plot above the GMWL, whereas the isotopic signatures of groundwater samples from the Beishan area fall below the GMWL and plot along the Zhangye LMWL.

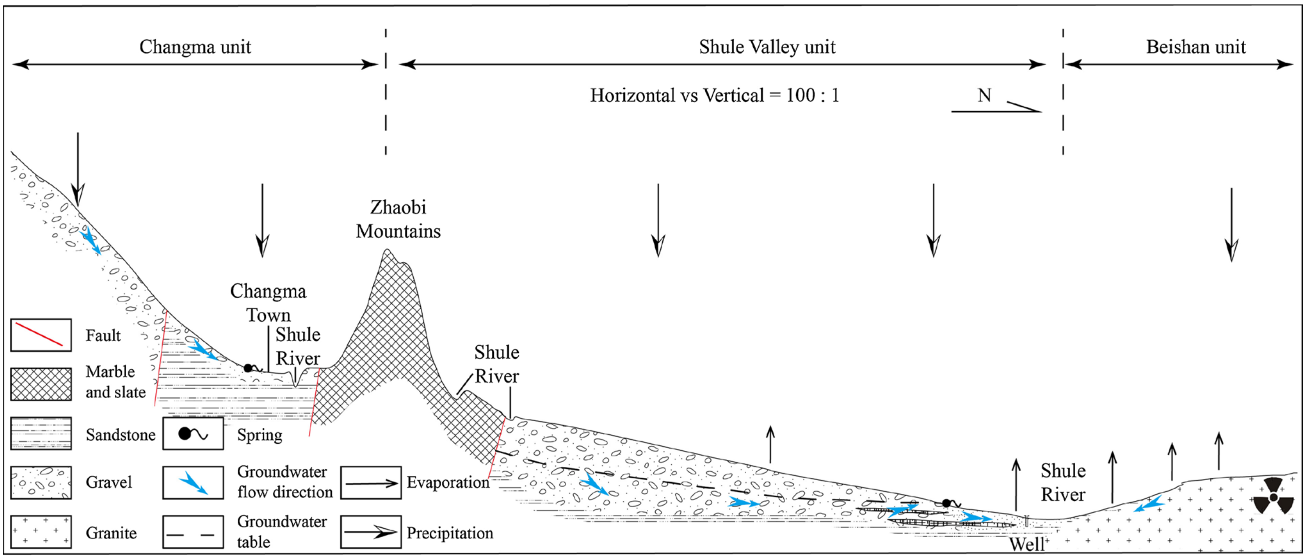

Fig. 8 Conceptual diagram of groundwater circulation in the study area

Minerals are dissolved continually by low-salinity groundwater along the flow path from Changma to the Shule valley. Groundwater salinity increases gradually from the recharge area to the discharge area in many other arid areas worldwide, including the Mayo Tsanaga River basin in western Africa (Fantong et al. 2009) and the Chari-Baguirmi depression, Republic of Chad (Abderamane et al. 2013). Based on the ion-ratio plot, rock weathering and dissolution are shown to be predominant factors controlling the major ionic composition. The Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- were likely derived primarily from the dissolution of calcite, dolomite, and gypsum, whereas halite provided equivalent amounts of Na^+ and Cl^-. Major ions have a stoichiometric ratio near 1 for Ca^{2+}+Mg^{2+} and $SO_4^{2-} + HCO_3^-$ and also a mNa/Cl ratio near 1. This has been observed in many of the neighboring basins in the Hexi Corridor (Chang and Wang 2010; Wang et al. 2002), as well as in other inland river basins in northwestern China, such as the Ejina basin (Wang et al. 2011; Gaofeng et al. 2010).

The scientific results presented here have important implications for groundwater management in the Shule River basin. Present day sources of water for recharge are relatively abundant; however, because glaciers are receding rapidly, recharge may be limited in future. In addition, groundwater in the Shule valley is derived from distant recharge sources. Exploitation of groundwater in the Shule River must be limited to plan for future water demands, to protect the fragile ecology of the arid land, and to sustain the region's socioeconomic development.

In the Beishan area, where the quality of available water is typically insufficient for use as drinking or irrigation water, local precipitation is the only possible source of recharge for groundwater. Because the permeability of the aquifer in Beishan is extremely low, the groundwater flow velocity in the region is slow; the resulting long residence times allow for more extensive water–rock interactions, including dissolution, exchange reactions, and concentration. Thus, the TDS of groundwater is generally high. Moreover, although the groundwater in the Beishan area continues to flow into the Shule valley under the influence of gravity according to theoretical analysis of groundwater flow system, groundwater itself is generally scarce in this region owing to geological and climatic constraints; accordingly, the amount of runoff from Beishan to the Shule valley is generally low. However, these factors do not negate the overall importance of the Beishan area: the region has been pre-selected for deep geological disposal of high-level radioactive waste, and the slow groundwater flow and limited runoff amounts are in fact desirable under these circumstances. Moreover, the observed poor hydraulic connection between the Beishan area and the Shule valley should hamper movement of radionuclides, thus ensuring the safety of the Shule valley groundwater.

Acknowledgments This research was supported by The High-Level Radioactive Waste Disposal Project of the State Administration for Science, Technology and Industry for National Defense, China. We thank the anonymous reviewers for their comments, which greatly improved the paper.

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