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Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China

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Summary A hydrochemical investigation was conducted in the Minqin Basin to identify the groundwater evolution and recharge in the aquifer. The mBr/Cl ratio is strongly depleted (average 0.000451) compared with sea water (0.0035), indicating an evaporite origin. The ionic ration plot, saturation index (SI), and chloro alkaline indices (CAI) suggest that the dissolution of halite, the glauberite, gypsum, dolomite and calcite determine Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- chemistry, but other processes, such as Na^+ exchange for Ca^{2+} and Mg^{2+}, and calcite precipitation also contribute to the water composition. The $\delta^{18}O$ and δ^2H in precipitation near the study area are linearly correlated, similar to that for the world meteoric water line (WMWL), with an equation of $\delta^2H = 7.49\delta^{18}O + 5.11$ ($r^2 = 0.97$). According to radiocarbon residence time estimates, the deep groundwater is approximately 40 ka old, and was recharged during a period when the climate was wetter and colder. The radiocarbon content of shallow groundwater shows a clear evolution along the groundwater flow path. From the beginning of the groundwater flow path to ~31 km the radiocarbon values are >73.6 pmc, whereas beyond this point the values are <42.9 pmc. Based on radiocarbon content, the shallow groundwater is older than 1 ka, and represents palaeowaters mixed with a limited quality of modern recharge.

The rain-fed groundwater direct recharge was estimated by chloride mass balance (CMB) method to range from 1.55 to 1.64 mm yr^{-1}, with a mean value of 1.6 mm yr^{-1}. This value represents about 1.5% of local rainfall. The direct recharge volumes is about 0.666×10^8 m^3 yr^{-1}.

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Indirect recharge volumes by the surface water is about 0.945×10^8 m^3 yr^{-1}. The total natural recharge in the Minqin Basin is 1.6×10^8 m^3 yr^{-1}, whereas the groundwater abstraction has reached 11.6×10^8 m^3 yr^{-1}, far exceeding the groundwater natural recharge.

Introduction

Northwest China, including the whole Xingjing autonomous region, the Hexi Corridor in Gansu Province, and the area west of Helan Mountains in Inner Mongolia, is one of the driest regions in the world (Shi and Zhang, 1995). This area is an ecologically fragile area, which is characterized by low and irregular rainfall, high temperatures and evaporation, and notable drought periods (Ma et al., 2005). In such arid and semi-arid environments, groundwater is a significant part of the total water resource, and plays an important role as a water supply both for drinking and irrigation. Because of rapid economic growth and lack of precipitation, the use of groundwater resources has increase dramatically. Substantial over-exploitation of groundwater has created serious consequences, for example, intense mineralization of groundwater, lowering of the regional water table, land desertification and salinization, degeneracy of vegetation and a heightened frequency of sand storms (Feng et al., 2005). If such a situation continues, further deterioration of the environment and ecosystem of the vast area is unavoidable. Some safeguarding measures for groundwater resource protection must been undertaken.

The Minqin Basin is located in the lower reach of the Shiyang River Basin. Already the water in the Shiyang River is over-used for irrigation and little or no surface water now reaches the Minqin Basin itself. As a result, farms in the Minqin Basin are now depending on the pumping of groundwater for both irrigation and drinking water. Recently, groundwater has begun to be exploited in the vicinal desert region, e.g. the Tengger desert. There can be little doubt the groundwater is being extracted much more rapidly than it is being replaced. Further more, the quality of groundwater may change as volume decline. Also this is an issue that faces the whole region of arid China (Ma et al., 2005).

Knowledge on the quality of groundwater and rate of recharge is important. During the last decades environmental isotope techniques have been commonly and largely used in the overall domain of water resources development and management (Fritz and Fontes, 1980). In fact, the application of these relatively new techniques has played an important role in solving the envisaged hydrological problems that cannot be solved by conventional methods alone. Stable isotopes, oxygen-18 (^{18}O) and deuterium (^{2}H) are commonly used for flow-system tracing and climate reconstruction. The chloride-mass balance (CMB) is used for groundwater recharge because of its conservative nature. Furthermore, the application of these techniques in the case of arid and semi-arid zones, where the available water resources are often limited to groundwater, has proved to be an attractive tool for the identification of recharge and the quantitative evaluation of groundwater system (IAEA, 1980, 1983). In recent years, the Chinese government and scientists have carried out much research on the assessment and utilization of water resources in the Shiyang River Basin. Many researches focus on the quantity assessment of natural water resources, understanding of the relationships between water and environment, and recognizing how to practice sound water management (Liu et al., 1998; Ye et al., 1998). However, study of the hydrochemistry (especially isotopic geochemistry) of water resources is rather sparse, and efforts to use the geochemistry data available to solve particular problems are even fewer or non-existent. This study combines the systematic analysis of the hydrochemical analysis and hydrogeologic features of the Shiyang River Basin with isotopic geochemical method for rainfall, surface water and groundwater in the Minqin Basin. The first goal of this study was to use minor elements (Br, B, Sr), environmental stable isotopes (^{18}O, ^{2}H, ^{13}C) and radiocarbon to determine the evolution and age of the groundwater in the natural conditions. The major-ion chemistry (Cl^-, HCO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+}) were employed to determine the predominant geochemical processes that take place along the groundwater flow path. Secondly, in order to determine the safe yield of the aquifer in Tengger desert, the chloride mass balance (CMB) method was used to calculate the recharge flux. The results of this study provide essential information and a theoretical basis for effective design of water resource management in northwest China in the new century.

The study area

The Minqin Basin is the lower reach of the Shiyang River system, which is located in the east Hexi Corridor of Gansu province (Fig. 1). It is approximately between latitudes 38°20′ to 39°18′ North and longitudes 102°52′ to 103°50′ East. The basin covers an area of 41.6×10^3 km^2. The Hongyashan Mountains, the tail of Longshou Shan Mountains, separate the Wuwei Basin and the Minqin Basin, where a reservoir was built in 1958 and is the only surface water in the Minqin Basin. Although the discharge of the Shiyang River at the mouth of mountain valleys has remained near 15.8×10^8 m^3 yr^{-1} since the 1950s, the flow into the lower reaches at the Hongyashan reservoir has decreased by 74% over the same period. In the 1950s, the discharge of the Shiyang River at Hongyanshan reservoir in the Minqin Basin was 5.73×10^8 m^3; in the 1960s, 4.45×10^8 m^3; in the 1970s, 3.22×10^8 m^3; in the 1980s, 2.25×10^8 m^3; and in the 1990s, only about 1.48×10^8 m^3 (Ma et al., 2005). As a result, groundwater recharge has greatly decreased by 75% from 0.48×10^9 m^3 yr^{-1} in the 1950s to 0.12×10^9 m^3 yr^{-1} in the 1990s (Li, 1983).

The Minqin Basin borders the Wuwei basin to the south, the Tengger desert to the east and north, and to the west

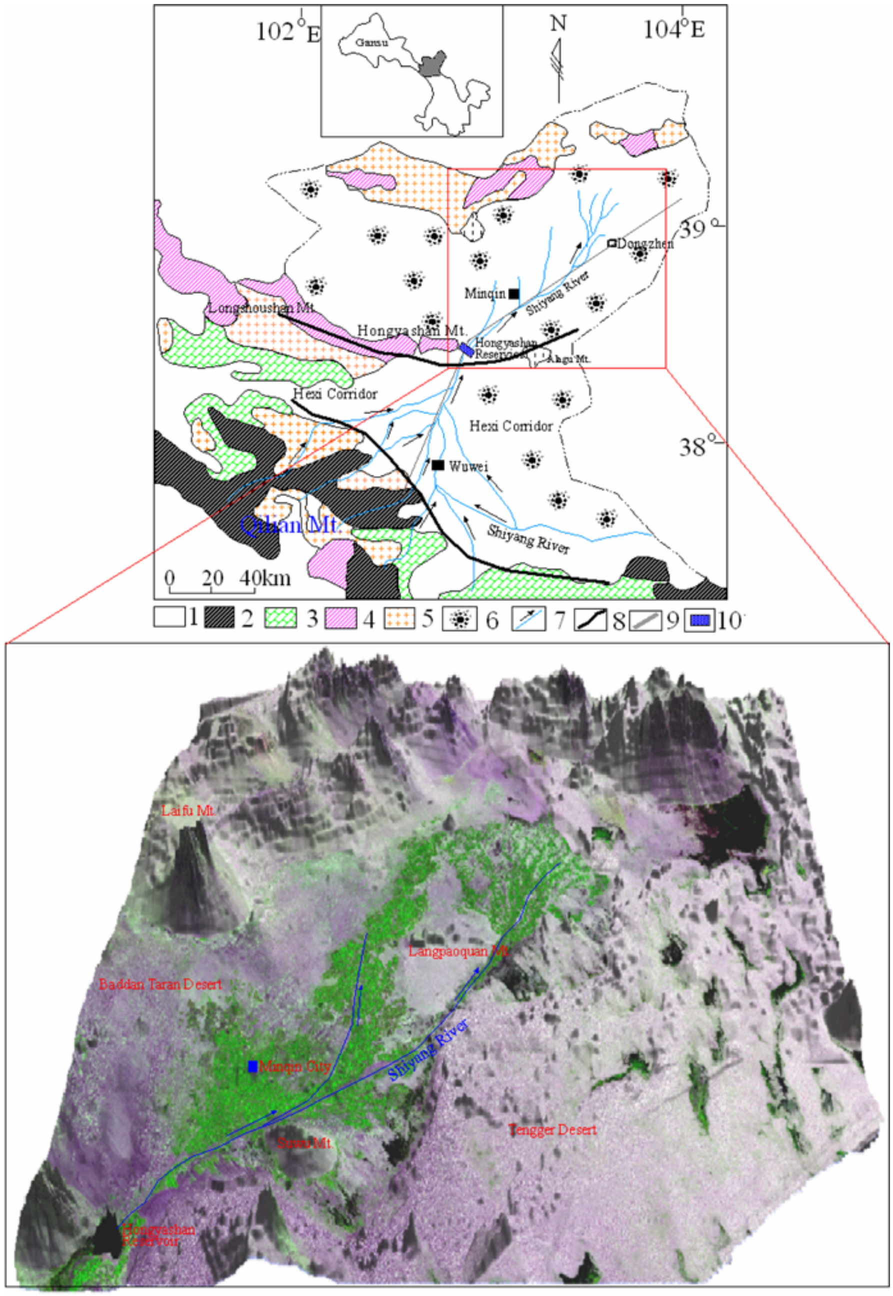

Figure 1 Location of the study area. 1 — subsilt and fluvial-lacustrine dastic; 2 — fluvial—lacustrine coarse clastics; 3 — marine limestones; 4 — metamorphic rocks; 5 — granite; 6 — desert; 7 — river and its flow direction; 8 — fault; 9 — cross section; 10 — Hongyashan reservoir.

the Baddan Taran desert and Longshoushan Mountain, with elevations that range from 1290 m to 1500 m. The climate of the study area is highly continental, with a long dry season from October to June, and a three-month rainy season from July to September, which contributes almost 66% of the total rainfall. The annual average precipitation is only 110 mm, whereas the potential evaporation is more than 2600 mm, which results in water scarcity. The average temperature is 7.8 °C, and winter temperature minima can fall to −27.3 °C whereas summer maxima rise to 41.1 °C. The diurnal temperature difference between day and night is 15.2 °C.

Geology and hydrogeology

The Shiyang River originates from Qilian Mountains (Fig. 1). The uplift of the Qilian Mountains occurred from the end of the Palaeozoic throughout the whole Mesozoic era, and created the embryonic form of the Hexi Corridor. This was followed by a complex tectonic stage when Longshoushan—Hongyashan structural zone was formed in the middle of the Hexi Corridor, cutting the whole Corridor into two parts: the southern Wuwei Basin and the northern Minqin Basin. From the late Tertiary, especially from the end of Pliocene and the beginning of the early Pleistocene, the surrounding mountains began to rise up rapidly (Li et al., 1979), and the Wuwei and Minqin basins subsided further. As a result of this period of activity, a series of NNW or NE faults were formed along the piedmont (Fig. 1). At the same time denudation from the mountains led to significant transfer of clastic material to the basin depression. Deposition of these clastics formed the Quaternary diluvial and alluvial sediments, and some aeolian and lacustrine sediments, which form the main aquifers.

In the southern part of the Shiyang River basin, the diluvial aquifer is composed of highly permeable cobble and gravel deposits, as much as 200–300 m thick, in which the water levels range between 50 m and 200 m below surface. The specific capacity is about 3–30 $l\,s^{-1}\,m^{-1}$, and the coefficient of permeability is as much as 100–600 $m\,d^{-1}$ (Qu, 1991). 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, which is comprised of inter-bedded cobble gravel, fine sand and clay, becomes confined or semi-confined with piezometric levels less than 5 m deep. In many places the groundwater then discharges as springs and streams.

Since Pliocene, the Minqin Basin filled with Pliocene and Quaternary sediments with thicknesses of several hundred meters. The Pliocene and early Pleistocene sediments in the basin are inter bedded sub-consolidated fluvio-lacustrine sands with thicknesses averaging 200–300 m. The overlaying middle and late Pleistocene sediments are composed of fluvial sands in the south of the basin, whereas in the north they comprise interbedded sandy clay and clay, ranging from 80 to 130 m thick. The lacustrine and fluvial deposits are rich in evaporates such as halite, gypsum, and sodium sulphate. The loose Quaternary sediments provide an ideal place for groundwater preservation. The groundwater systems can be basically divided into two groups: the shallow phreatic aquifer and the deep confined aquifer (Fig. 2). The 70–100 m thick of the shallow phreatic aquifer is composed of middle and late Pleistocene sediments, and forms the main aquifer. The specific capacities of this aquifer range from 10 to 11 $s^{-1}\,m^{-1}$, and the coefficients of permeability range from about 70 to 10 $m\,d^{-1}$ along the groundwater flow direction (Qu, 1991). The buried depth of groundwater in the deep confined aquifer is more than 100 m. The aquifer is made up of early Pleistocene and Pliocene sediments.

Groundwater in the Minqin Basin is recharge by surface water via river infiltration, canal system seepage and farmland irrigation water seepage and infiltrating meteoric water in the basin. It is discharged mainly via evapotranspiration and artificial abstraction. The general direction of groundwater flow is from south to north.

Methods

Field investigation was carried out during September and October, 2002. A total of 23 groundwater samples were obtained from active water supply boreholes penetrating different lithological units in the Minqin Basin (Table 2; Fig. 2) and these fell into two distinct groups (shallow wells with depths <100 m, and deep wells with depths ranging from 200 m to 300 m), and two surface water samples from the Hongyashan reservoir were also collected for an initial reconnaissance of chemical and isotopic parameters. The location of sampling sites is shown in Fig. 3.

Alkalinity and physical parameters such as electrical conductivity (EC), pH, temperature, and redox potential (Eh) were measured in the field using an in-line flow cell to ensure the exclusion of atmospheric contamination and to

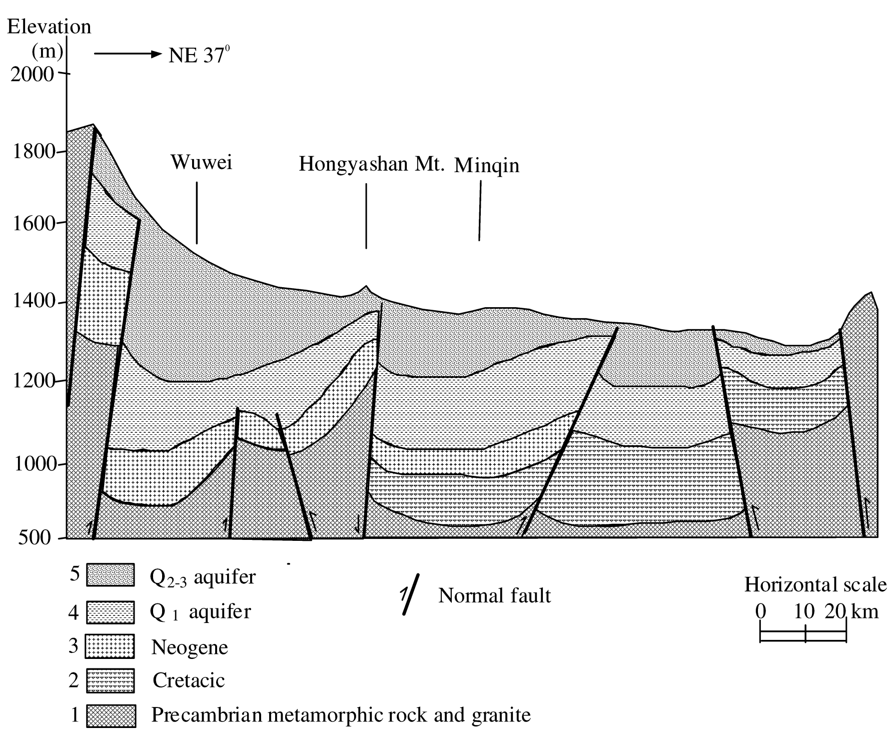

Figure 2 Geological cross-section of Shiyang River Basin along the line shown in Fig. 1.

improve measurement stability. Alkalinity was measured using a Hach® field titration kit. The EC, pH, temperature and Eh was measured using portable Orion EC and pH meters. Groundwater was collected after purging the wells for 15–20 min. Three filtered (0.45 μm) samples were taken at each site in acid-washed, well rinsed low density polyethylene bottles. One sample for major cation and trace element determination was acidified to make 1% in HNO_3^-, producing a pH around 1.5 sufficient to stabilize trace metals; filtered, unacidified samples were collected for anion analysis; and unfiltered samples were collected for isotope analysis. In 14 wells, the activities of ^{14}C and $\delta^{13}C$ were measured.

All inorganic and stable isotope analyses were carried out at the activation lab in Lanzhou, China. Major cation concentrations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) together with SO_4^{2-} (measured as total S), Si and Sr were analyzed using inductively coupled plasma-atomic emission spectrometer (ICP–AES). The accuracy of ICP–AES analyses was controlled using appropriate laboratory standards and checked during each batch using international reference standards. Anion concentrations (Cl^-, SO_4^{2-}, NO_3^-, and Br^-) were determined by automated colorimetry. The analytical precision for measurement of ions was determined by calculating the ionic balance error, which is within 5%.

The analysis of light isotopes (O, H, C) in the water samples was carried out by mass spectrometry (VG Micromass 602C) and radiocarbon was determined by accelerator mass spectrometry (AMS) at the Geological Scientific Research Institute of China. All stable isotopic composition (^{18}O, D, and ^{13}C) are reported in standard δ notation in which $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, where R_{sample} and $R_{standard}$ represent the ratio of heavy to light isotopes of the sample and standard, respectively. The results of radiocarbon are reported as pmc (percent modern carbon). The analytical reproducibility is 0.1‰ for $\delta^{18}O$, and ±1% for δD, $\delta^{13}C$, and ^{14}C.

Two augur profiles were drilled by hand at Beitu, to the southeast of the Minqin Basin, to obtain samples for chloride

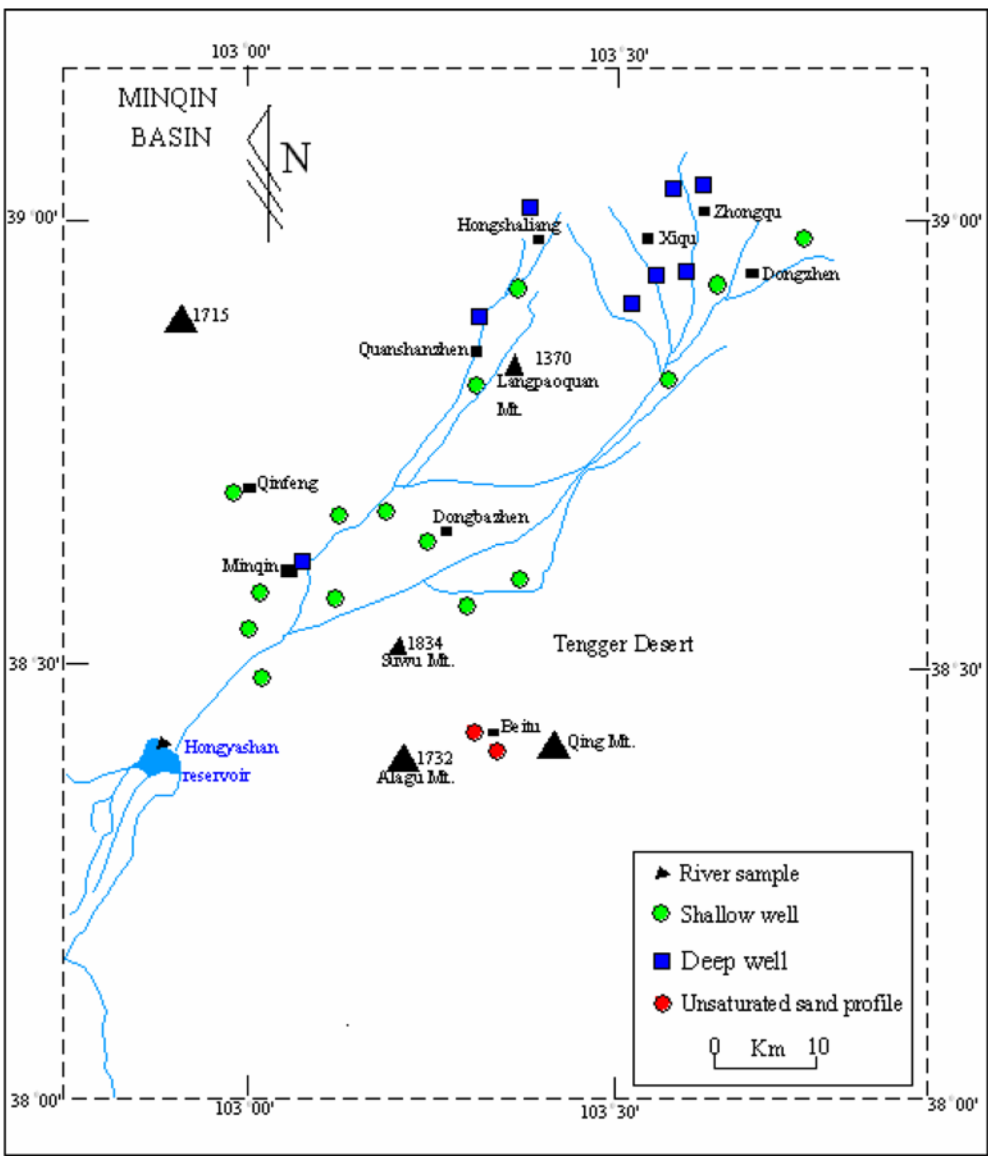

Figure 3 Sampling well sites of the study area with two augur profiles for Chloride analysis.

analysis from unsaturated zone (Fig. 3). In this region, there are no perennial rivers, and groundwater storage in the alluvial aquifer depends on direct recharge from precipitation. The chloride-mass balance (CMB) method was used to estimate modern recharge rates. Chloride can reasonably be regarded as a conservative element in the shallow hydrological cycle because it derived from atmospheric deposition. The relation between rainfall and recharge (Ting et al., 1998; Wood, 1999) is

$$q = R_{\mathrm{eff}}\mathrm{Cl}_{\mathrm{p}}/\mathrm{Cl}_{\mathrm{sm}}$$

where q is the recharge (mm yr^{-1}), R_{eff} is the effective rainfall (mm yr^{-1}), Cl_{p} is the average concentration of chloride of rainfall (mg/l). $\mathrm{Cl}_{\mathrm{sm}}$ is the average concentration of chloride (mg/l) over the profile in the unsaturated zone. The application of the technique in the case of arid and semi-arid zones is very attractive as a tool for the quantification of recharge rates to groundwater systems (IAEA, 1980, 1983; Clark and Fritz, 1997).

Results and discussion

Groundwater evolution along the flow path — major element trends

Range, mean values and standard deviation of the physical parameters (pH, temperature, EC and Eh) and the saturation index for gypsum and calcite are shown in Table 1. The chemical and stable isotope (δ^{18}O and δD) composition of 23 groundwater samples and two surface water samples as well as ^{14}C and δ^{13}C composition of 14 groundwater samples are presented in Table 2. The pH value ranges from 6.74 to 9.65 with an average value of 8.14. Trends of groundwater chemistry along its flow paths may give clues to the hydrochemical processes prevailing in the Minqin Basin (Rosen and Jones, 1998). A series of plots illustrate the key hydrochemical trends along the groundwater flow path (Figs. 4 and 5). The EC values of the groundwater is low in the southern part of the study area and there is a gradual increase along the groundwater flow path due to the long residence time of the water in the rock and high ambient temperature (Feng et al., 2005). The behaviors of ion concentrations, in general, are similar with the EC values of the groundwater. However, in the final reach of the study area the concentration of SO_4^{2+}, Cl^-, Na^+ and Mg^{2+} increase more prominently than others (Fig. 4). Chloride is used as a conservative reference element against which to study the water-rock interaction. Chloride concentrations are typically between 63.6 and 247 mg/l at the initial 45 km of the groundwater flow path (Fig. 4) and at the lower reach of the basin are variable between 129 and 1100 mg/l. The groundwater is generally fresh (TDS <1000 mg/l) with Cl^- below 250 mg/l. A principal feature of the groundwater is the enrichment in Na^+ relative to Cl^- (Fig. 5) giving molar ratios up to 2 in the initial 45 km of the groundwater flow path, although beyond this point the higher salinities of the groundwater mask the effect to give slightly lower values. The high mNa/Cl ratios are indicative of strong water-rock interaction. SO_4^{2-} exhibits a similar evolution pattern with Cl^- with more enrichment (average wt $SO_4^{2-}/Cl^- = 2.55$) (Fig. 5). The other major anion HCO_3^- varies slightly, ranging from 163 to 948 mg/l with a mean value of 285.83 mg/l. Among the cations, Na^+ is dominant in the groundwater. One significant characteristic of the groundwater is very low K^+/Na^+ ratio of 0.03 (wt). The low levels of potassium in natural waters are a consequence of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals. Another feature is the significant enrichment in mMg/Ca (Fig. 5). An extreme composition is found in the lower reach sample (site S15) which has Ca: 287 and Mg: 477.0 mg/l, respectively. The main source of magnesium in groundwater is dissolution of dolomite which is common in sedimentary rocks in the Minqin Basin.

The origin and evolution of groundwater

Major and trace elements

The Br/Cl ratio is commonly used as an indicator for the origin of salinity, with values exceeding or equal to the marine ratio (average 0.0035) likely to originate from marine water or marine formation waters; whereas values much lower than the marine ratio indicate an evaporite source (Sanders, 1991; Richer and Kreitler, 1993).The plot of Br/Cl for the water of Minqin Basin (Fig. 5) indicates an evaporite origin for the groundwater with a strongly depleted ratio (average 0.000451). Surface water collected with Hongyashan reservoir is slightly enriched (average 0.000616) compared with groundwater. Surface water pollution is responsible for the high concentrations of Br, which may derive from methyl bromides and other organic bromyl

Table 1 Statistical descriptive for physical parameters and saturation indices of groundwater in the study area

	Shallow groundwater				Deep groundwater			
	Min.	Max.	Mean	Std. Dev.	Min.	Max.	Mean	Std. Dev.
pH	6.74	9.65	8.35	0.75	6.82	9	7.74	0.71
Temp. (°C)	9.8	13	10.7	0.8	11.2	13.8	12.3	1
EC (*us*/cm)	1316	9520	3370.6	2314.8	1401	6520	1942.1	3231.4
Eh (mv)	−251	19	−72.4	84.4	−107	37	−14.7	51.7
$SI_{Calcite}$	0.4	1.85	1.26	0.29	0.73	1.34	1.02	0.23
SI_{gypsu}	−1.79	−0.36	−0.89	0.32	−1.43	−0.44	−1.01	0.37

$SI_{Calcite}$: Saturation indices for calcite.
SI_{gypsum}: Saturation indices for gypsum.

Table 2 Chemical and isotopic composition of samples in the study area

Map No.	Lithology	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	SiO_2 (mg/l)	Br (mg/l)	Sr (mg/l)	$\delta^{18}O$ (‰)	δD (‰)	^{14}C (pmc)	$\delta^{13}C$ (‰)	Apparent ages (ka)
S1	5	90	403	300	95.8	4.4	115	75	7.24	0.04	1.58	−7.51	−53.7	84.5	−9.8	1.4
S2	5	63.6	238	262	70.4	4.6	85.5	41.3	7.28	0.04	1.28	−7.64	−56.2	–	–	–
S3	5	151	511	298	171	8.6	119	87	7.53	0.11	1.91	−8.83	−55.1	–	–	–
S4	5	207	283	181	286	3.9	20.4	12.7	5.89	0.04	0.436	−10.17	−71.9	–	–	–
S5	5	157	562	336	175	6.2	145	83	7.25	0.08	2.19	−7.38	−55.0	80.6	−7.8	1.8
S6	5	226	718	302	191	8.2	181	108	7.37	0.10	3.15	−8.78	−57.8	74.2	−7.9	2.4
D1	5,4	115	324	213	93.7	5.5	108	51.4	7.25	0.07	1.46	−11.28	−73.1	73.7	−9.3	2.5
S7	5	223	758	350	247	9.1	130	109	7.06	0.13	2.37	−9.06	−57.4	–	–	–
S8	5	120	404	252	130	5.8	113	54.7	7.2	0.07	1.5	−8.03	−58.1	–	–	–
S9	5	125	442	226	164	5.1	118	52.8	6.87	0.07	1.49	−8.40	−61.2	73.6	−7.3	2.5
S10	5	247	659	314	243	7.3	132	97	7.1	0.12	2.19	−7.94	−57.8	65.8	−5.9	3.4
S11	5	210	693	163	181	5.3	167	72	8.67	0.11	2.26	−8.38	−57.7	42.9	−6.0	6.9
S12	5	509	675	190	301	5.3	169	99	7.8	0.07	2.78	−9.68	−60.3	–	–	
D2	5,4	129	293	150	135	2.7	52.3	38.2	6.95	0.03	1.47	−10.35	−69.3	10.65	−6.9	18.5
D3	5,4	369	311	156	276	2.8	67.4	59.3	6.15	0.08	2.5	−10.45	−67.3	8.9	−8.0	20.0
S13	5	325	938	382	319	5.4	129	135	7.19	0.27	2.5	−8.99	−59.9	–	–	
S14	5	1100	1400	390	1060	8.6	145	136	7.22	0.20	3.0	−8.89	−59.7	–	–	
D4	5,4	208	306	202	216	4.3	48.4	36.9	5.76	0.10	1.99	−9.5	−65	6.3	−7.7	22.9
D5	5,4	860	992	172	533	3.8	182	164	5.86	0.18	7.99	−10.13	−67.9	5.4	−7.9	24.1
S15	5	1060	2330	948	822	28.6	287	477	9.63	0.39	5.37	−2.95	−31.6	–	–	
D6	5,4	420	1130	163	413	3.7	260	123	6.1	0.21	8.94	−10.29	−68.5	2.7	−8.0	29.9
D7	5,4	339	512	159	257	2.5	89.9	78	6.56	0.14	4.73	−10.39	−68.6	0.66	−8.3	41.5
D8	5,4	630	1400	465	514	5.3	130	238	6.48	0.33	4.69	−8.85	−61.8	7.6	−8.7	21.3
Reservoir	–	57.4	224	156	71.5	11.4	48.1	33.4	3.16	0.07	0.88	−3.1	−27	–	–	
Lake	–	1550	2370	35.9	1090	62	655	39.8	1.22	0.02	Saturated	1.7	−4	–	–	

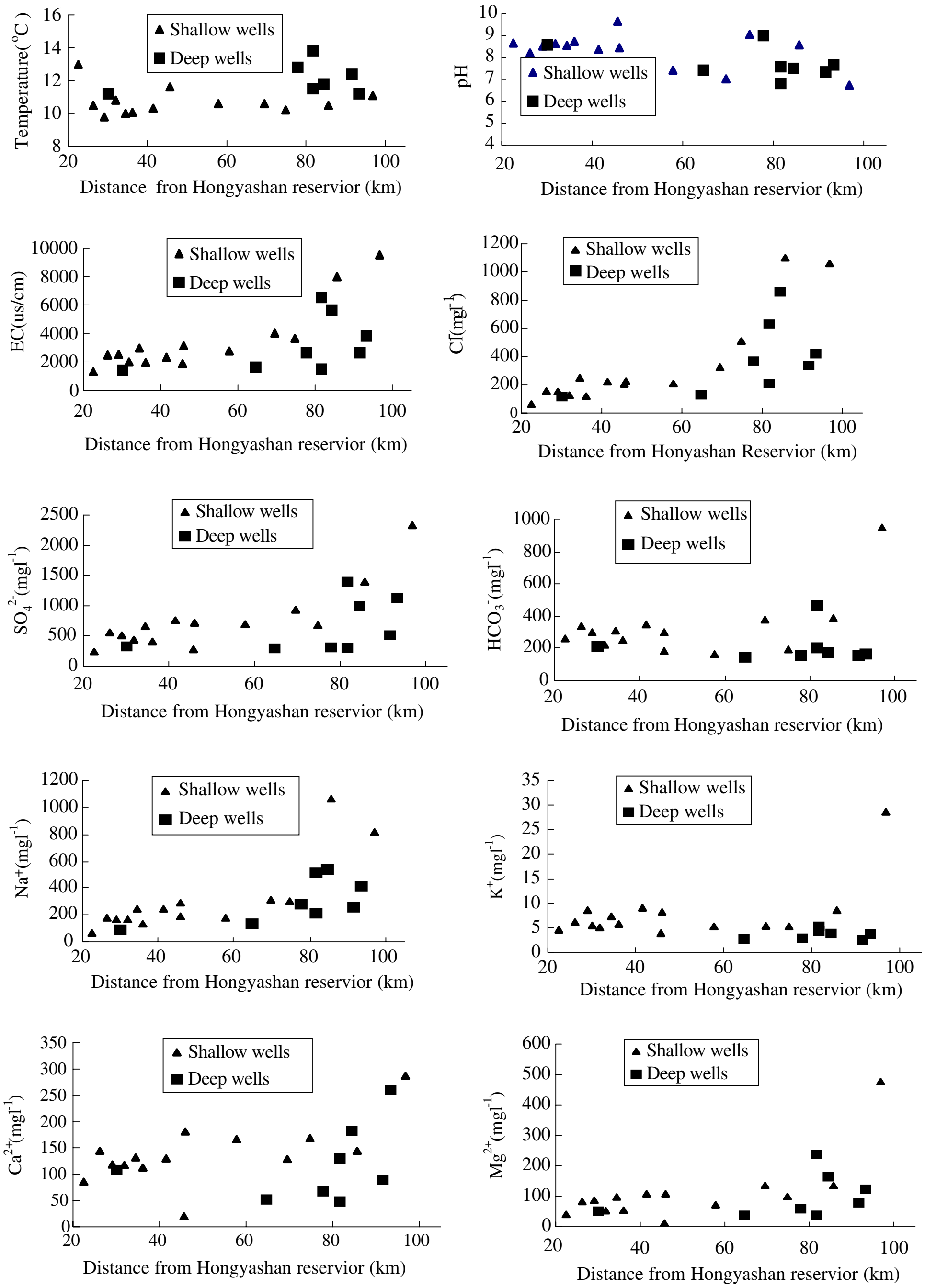

Figure 4 Physical parameters (pH, temperature and EC) and major irons variations along the distance from Hongyashan reservoir.

components used in agricultural (Vengosh and Pankrator, 1998).

The plot of Na vs Cl can be used as a first order indicator of water—rock interaction. Although Na^+ and Cl^- exhibit a good correlation (Fig. 5), halite dissolution may exert a control on the Na^+ and Cl^- chemistry. In the initial 45 km of the groundwater flow path the groundwater has high Na/Cl molar ratio up to 2.13 (site S4) (Fig. 5). Some sodium may be derived from Na-bearing silicate minerals, such as albite. Weathering of albite produces kaolinite and Na^+ ions. This reaction would result in a Si/(Na—Cl) of ±2. The Si/(Na—Cl) ratio encountered in the Minqin Basin is generally lower than 2 (Fig. 4). As no silicate weathering reaction could explain such low ratios (Stallard and Edmond, 1987), the excess Na^+ is probably not derived solely from silicate weathering. A good linear relationship between Na^+ and SO_4^{2-} suggests the dissolution of Glauber's salt. If the dissolution of Na_2SO_4 is a main process, the plot of Na^+—Cl^- vs SO_4^{2-}—Ca^{2+} + Mg^{2+} should have a slope of 1. All data plot, as expected, a little lower than the line of slope 1 (Fig. 5). Sediment core from a borehole near the terminal lake area contain Glauber's salt. The groundwater collected from the lower reaches has Na/Cl molar ratios that are close or even below 1 (Fig. 5). The trend shows that the dilution with halite most probably causes the convergence in the saline waters. In addition, the relative high concentration of

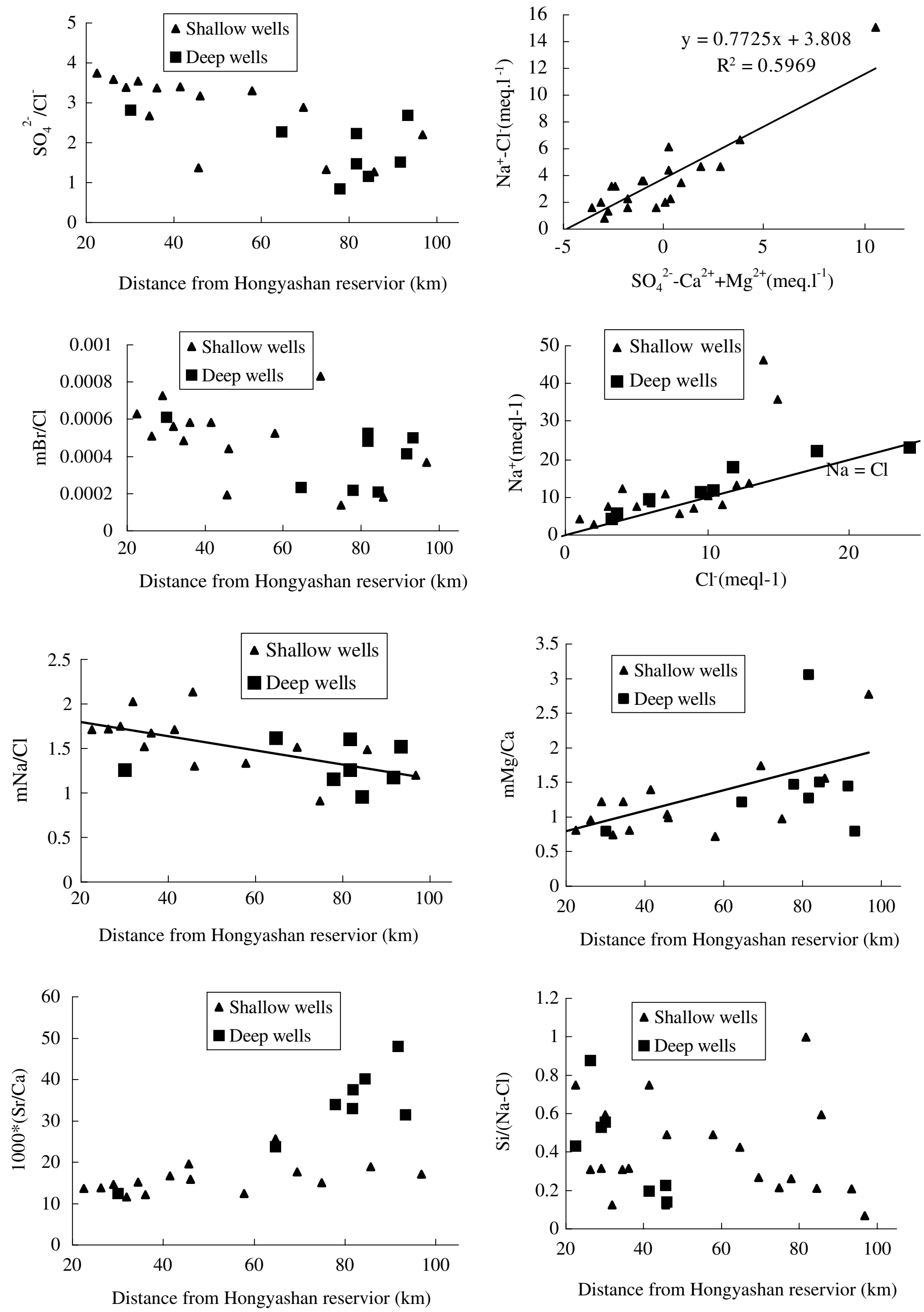

Figure 5 Major ion relationships (SO_4/Cl, (Na—Cl)/(SO_4—Ca + Mg), Br/Cl, Na/Cl, Mg/Ca, Sr/Ca and Si/(Na—Cl)) along the distance from the Hongyashan reservoir.

Na^+ may promote the reverse ion exchange (discussed below).

In the study area, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} mainly derived from the dissolution of gypsum, dolomite, and calcite. The high Mg/Ca molar ratio (Fig. 5) strongly indicates that weathering of dolomite or carbonates containing high concentration of Mg^{2+} may be important. Strontium is typically derived from carbonate or sulphate salts (Vitousek et al., 1999; Fairchild et al., 2000). The relative high Sr/Ca molar ratio (Fig. 5) seen in the groundwater tends to occur in solutions that have precipitated calcite. Precipitation of $CaCO_3$ is also supported by the generally positive saturation indices (SI) for calcite. The calculated values of SI for calcite of the groundwater samples range from 0.4 to 1.85 with a mean values of 1.26 (Table 1).

The Na/Ca molar ratio increases along the groundwater flow path. The existence of abundant Na^+ may promote cation exchange. This is confirmed by two indices of base exchange (IBE), namely the chloro alkaline indices (CAI 1 and CAI 2) (Schoeller, 1965).

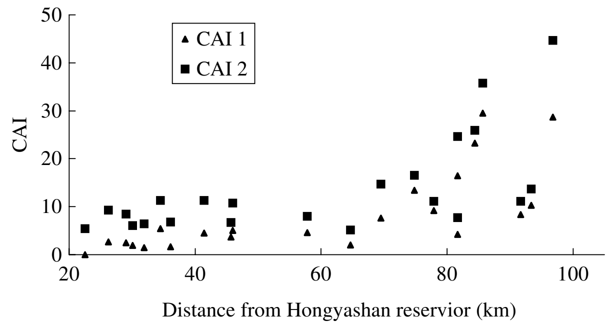

Figure 6 Variation of groundwater chloro alkaline indices (CAI) along the distance from Hongyashan reservoir.

$$\text{CAI} \quad 1 = \text{Cl} - \frac{\text{Na} + \text{K}}{\text{Cl}}$$

$$\text{CAI} \quad 2 = \text{Cl} - \frac{\text{Na} + \text{K}}{\text{SO}_4} + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3$$

When there is an exchange between Na or K in groundwater with Mg or Ca in the aquifer material, both of the indices are positive, indicating ion exchange of sodium in groundwater with calcium or magnesium in the alluvium or weathered materials. In the study area these indices are all positive (Fig. 6). So the ion exchange reactions seem to occur along the groundwater flow path.

In summaries, the salinity of the groundwater slightly increases along its flow path due to the long residence time of the water in the rock and high ambient temperature. The high Na/Cl molar ratio and a good liner relationship between Na^+ and SO_4^{2-} in the initial 45 km of the groundwater flow path are indicative of dissolution of Glauber's salt, whereas in the lower reaches the dilution with halite causes the convergence in the saline waters to give slightly lower values. The higher Sr/Ca molar ratio and positive saturation indices for calcite suggest that the precipitation of $CaCO_3$ may occur in the groundwater. The high Mg/Ca molar ratio strongly indicates that weathering of dolomite or carbonates containing high concentration of Mg^{2+} may be important. In addition, the positive values of the chloro alkaline indices suggest ion exchange of sodium in groundwater with calcium or magnesium in the alluvium or weathered materials.

Isotope geochemistry

The environment isotopes of oxygen δ^{18}O and hydrogen δ^2H are excellent tracers for determining the origin of groundwater and widely used in studying the natural water circulation and groundwater movement (Ali, 2004). The isotope composition of groundwater, surface water and precipitation at several meteorological stations around the study area (including Lanzhou, Yinchuan, Lasha and Zhangye from the IAEA database) are plotted in Fig. 7 and listed in Table 2. The δ^{18}O and δ^2H in precipitation range between $-191‰$ and $5‰$ and between $-24.7‰$ and $3.8‰$, respectively, but they are linearly similar to the world meteoric water line (WMWL) with an equation of $\delta^2H = 7.49\delta^{18}O + 5.11$ ($r^2 = 0.97$). Several values are slightly enriched in δ^{18}O relative to the WMWL and indicate modification due to evaporation. The weighted mean δ^{18}O value of rainfall at Zhangye Station (located 150 km west of the Minqin Basin) lies around $-7‰$, and these values can be taken as representive of present day local waters. The δ^{18}O compositions of the surface water from Hongyashan reservoir, which is slightly evaporated, range between $-3.1‰$ and $1.7‰$. This tend towards heavier values of δ^{18}O is typical phenomenon prior to recharge in semi-arid and arid areas (Gat, 1981). The shallow groundwater has δ^{18}O values in the range of $-9.68‰$ to $-7.14‰$ and δ^2H from $-61.2‰$ to $-51.4‰$. The average values of δ^{18}O and δ^2H in the shallow groundwater are $-8.31‰$ and $-57.27‰$, respectively. The deep groundwater has δ^{18}O values in the range of $-11.28‰$ to $-8.85‰$ and δ^2H from $-73.1‰$ to $-61.8‰$. The average values of δ^{18}O and δ^2H in the deep groundwater are $-10.16‰$ and $-68.69‰$, respectively.

Several observations may be made about the stable isotopes in the groundwater in relation to the surface water as well as the modern rainfall. Firstly the groundwaters

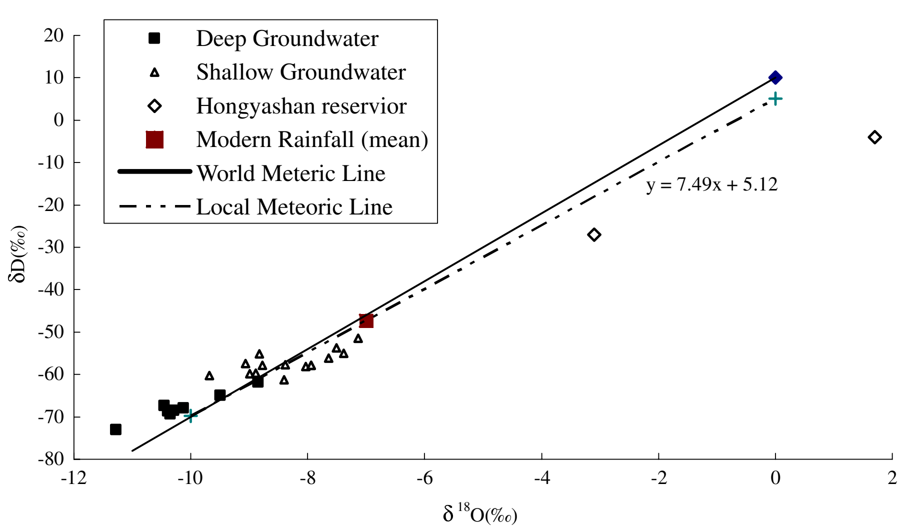

Figure 7 Plot of δ^{18}O and δD for groundwater from Minqin Basin aquifer system with plots of precipitation around the Minqin Basin and Hongyashan reservoir water trends.

are following the WMWL (Fig. 7). This indicates that the groundwater recharge resources mainly source from precipitation. Secondly the groundwater is strongly depleted in both ^{18}O and ^{2}H relative to modern rainfall by up to 3.16‰ in ^{18}O. Thirdly the deep groundwater is notably depleted in heavy isotopes in comparison with shallow groundwater (Fig. 7), suggestive of cooler recharge conditions than at present day.

Radiocarbon activities were measured on 14 selected samples to establish the groundwater residence time (Table 2) using the Pearson model (Fontes and Garnier, 1979) in which the measured $\delta^{13}C$ values have enabled corrections to be made, using a value of 100% modern carbon together with a soil CO_2 value of $-26‰$ and carbon of 0.8‰. The radiocarbon values, expressed as percent modern carbon, (pmc) exhibit a range from 0.66 to 84.5. The deep groundwater samples have values of less than 10.65 pmc, indicating a predominance of ancient recharge. There is one exception (site D1) with a higher value of 73.7 pmc, which maybe a result of mixing with modern water. The deep groundwater is old, approximately 40 ka. In contrast, the radioisotopes data of shallow groundwater show a clear evolution along the groundwater flow path. From the beginning of the groundwater flow path to ~31 km the shallow groundwater have values more than 73.6 pmc with ages less than 3.5 ka. At 46 km along the groundwater flow path the value is 42.9 pmc with an age of 6.9 ka. The shallow groundwater is younger but generally older than 1 ka, and likely represents a mixture of palaowaters limited modern recharge.

Recharge to the aquifer

Recently, production wells have been drilled in the vicinal desert region to meet the increasing water demand of domestic, irrigation and industrial activities. In the desert region away from streams groundwater is recharged by precipitation directly. The chloride-mass balance (CMB) method is applied to estimate the recharge flux for the aquifers. Based on the data of the Minqin Meteorological Station for the period 1957—1999 and the author's own field measurements, the regional effective annual rainfall (R_{eff}) is 110 mm, and the Cl^- concentration in rainfall (C_p) is 1.5 mg/l.

The regional effective annual rainfall (R_{eff}), the Cl concentration in rainfall (C_p), and the mean chloride concentration in the profile (C_{sm}) are summarized in Table 3. The estimation rate of recharge rang from 1.55 to 1.64 mm yr^{-1}, with a mean value of 1.6 mm yr^{-1}. This value represents about 1.5% of rainfall, which is acceptable for arid and semi-arid regions.

Groundwater recharge in the Minqin Basin takes place either as indirect recharge by the surface water via river infiltration, canal system seepage and farmland irrigation water seepage, or as widespread direct infiltration through the soil. Both processes are important and both contribute to the total recharge. Indirect recharge by the surface water in the Minqin Basin is about 0.945×10^8 m^3 yr^{-1} (Ma and Wei, 2003), whereas direct infiltration calculated by the CMB method is about 0.666×10^8 m^3 yr^{-1}. The total natural recharge in the Minqin Basin is 1.6×10^8 m^3 yr^{-1}, whereas the groundwater abstraction has reached 11.6×10^8 m^3 yr^{-1} (Ma et al., 2005), far exceeding the groundwater natural recharge.

Conclusions

In the Shiyang river basin, as in other large inland basins of NW China, large volumes of unconsolidated Late Pliocene and Quaternary sediments were deposited in the foreland depression, creating large and high storage aquifers. A hydrochemical investigation was carried out to identify the origin and evolution of the groundwater in one such basin-the Minqin Basin. Groundwater in arid regions is generally characterized by high ion concentrations, and the dominant anion species of water changes systematically from HCO_3^-, SO_4^{2-} to Cl^- along groundwater flow direction from the recharge area to the discharge area (Ronit et al., 1997). This situation has been observed in arid basins around the world such as northern Sahara sedimentary basin, Algeria (Guendouz et al., 2003); as well as other inland river basins in northwestern China such as Ejina Basin (Wen et al., in press) and Datong Basin (Guo and Wang, 2004). As shown in this study, the EC and the major ion concentration gradually increase along the groundwater flow direction, due to higher ambient temperature, water-rock interaction, and greater length of flow path. In the Minqin Basin, Na^+ is dominant among the cations, and SO_4^{2-} is more enrichment than other anions. The plot of Br/Cl for the water of Minqin Basin indicates an evaporite origin for the groundwater with a strongly depleted ratio relative to sea water. As in other continental-scale catchments, lithology plays a significant role in determining the major element hydrochemistry of groundwater in Minqin Basin. Although Na^+ and Cl^- exhibit a good correlation, suggesting that evaporation and halite dissolution may exert a control on the Na^+ and Cl^- chemistry, a high concentration of Na^+ and SO_4^{2-} relative to Ca^{2+} and Cl^- indicates the dissolution of Glauber's salt. The dissolution of gypsum, dolomite and calcite determine Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^- chemistry, but other processes, such as Na^+ exchange for Ca^{2+} and Mg^{2+}, and calcite precipitation also contribute to the water composition.

The $\delta^{18}O$ and δ^2H in precipitation in the study area are linearly correlated, similar to the world meteoric water line (WMWL) with an equation of $\delta^2H = 7.49\delta^{18}O + 5.11$ ($r^2 = 0.97$). Based on radiocarbon dates, the deep groundwater is old water, approximately 40 ka, and was recharged

Table 3 The estimates of mean annual recharge using chloride for β_1 and β_2 profiles

Profile	Sampling interval (m)	Mean rainfall (mm)	Mean Cl concentration in rainfall (mg/l)	Mean Cl in profile (mg/l)	Mean recharge (mm)
β_1	0—8.4	110	1.5	100.4	1.64
β_2	0—11	110	1.5	106.2	1.55

during a period when climate was wetter and colder. The shallow groundwater is younger but generally older than 1 ka, and likely represents a mixture of palaeowaters limited modern recharge. Based on radiocarbon and tritium values, Chen et al. (2004) established the deep confined groundwater ages of the Heihe River Basin in northwestern China range between 5.5 and 8.6 ka. The residence time of the groundwater in the Continental Intercalaire aquifer of North Africa is possibly up to 100 ka (Edmunds et al., 2003). In these arid basins around the world, the deep groundwaters are palaeowaters, and are non-renewable resource.

To determine the safe yield of the groundwater, a reliable estimate of groundwater recharge is needed for sustainable groundwater resources management. The CMB has been commonly used in the overall domain of water resources development and management (Wood, 1999; Kattan, 2001). Cater and others (1994) summarize previous rain-fed groundwater recharge studies in semi-arid and arid regions around the world. The groundwater recharge percentage of these studies range from 1% to 30% of the local rainfall. In our study, the estimation rate of recharge rang from 1.55 to 1.64 mm yr^{-1}, with a mean value of 1.6 mm yr^{-1}. This value represents about 1.5% of local rainfall. By 2000, the number of wells in the Minqin Basin had reached 10,000 and groundwater abstraction hand reaches $11.6 \times 10^8\ m^3\ yr^{-1}$ (Ma et al., 2005), far exceeding the $1.6 \times 10^8\ m^3\ yr^{-1}$ groundwater natural recharge. The exploitation of groundwater from the basin must be effectively regarded as development of a non-renewable resource, a fact that is indicated by the decline in piezometric heads within the basin. At present the water level has dropped widely by between 3 and 5 m with a maximum of 35 m in the Minqin Basin (Ma et al., 2005).

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