

# Hydrochemical Characterization of a Groundwater Aquifer and its Water Quality in Relation to Irrigation in the Jinghuiqu Irrigation District of China

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**ABSTRACT:** The Jinghuiqu irrigation district is located in the semi-arid regions of northwestern China, where groundwater is the most important natural source for local industry, agriculture and residents. The present work was conducted in the Jinghuiqu irrigation district to characterize the groundwater aquifer, which has undergone long-term flood irrigation for over 2000 years. Isotopic and hydrochemical analyses, along with geological and hydrogeological tools, were used to determine the chemical properties and evolutionary processes of the groundwater aquifer. Results showed that the groundwater chemistry had changed significantly from 1990 to 2009. Water with concentrations of CaMgSO<sub>4</sub> had decreased significantly, from 60% to 28% of the total water samples, during the period, while water with concentrations of NaSO<sub>4</sub> and NaCl increased significantly, from 28% to 72%. The salinity of the groundwater increased rapidly and the affected area had expanded to most of the irrigation district. Stable isotope studies showed that most of the groundwater concentrations were derived from sulfate mineral dissolution. The minerals saturation indices (SI), ion ratios and oxygen isotope values of the groundwater indicated that the shallow groundwater had mainly experienced mineral dissolution, cation exchange, and mixing of the irrigated surface waters and groundwater. The groundwater quality had continuously evolved toward salinization as concentrations of SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup> grew to dominate it. Water quality risk analyses showed that most of the saline groundwater is not suitable for domestic and irrigation uses, especially in the middle and eastern parts of the irrigation district. These findings indicate that the irrigation district should strengthen the groundwater resources management. *Water Environ. Res.*, 85, 245 (2013).

**KEYWORDS:** Geochemical characterization, Stable isotope, Jinghuiqu irrigation district.

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## Introduction

Groundwater pollution is one of the most important and widespread environmental problems in irrigated agricultural regions (Aber et al., 2003; El et al., 2007; Galloway et al., 2008).

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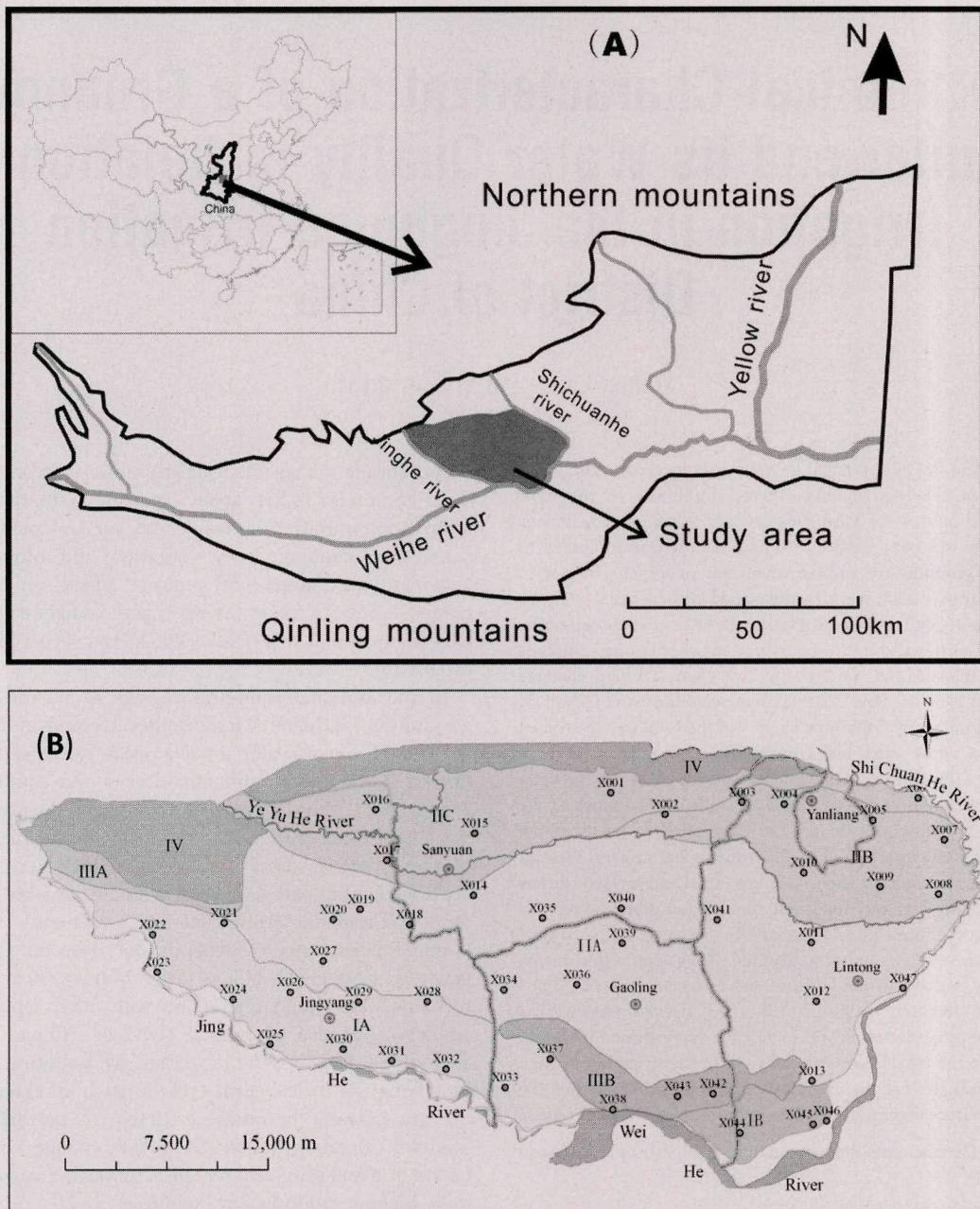
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Inappropriate management of groundwater promotes the rapid deterioration of water quality, putting both the human and animal communities at health and survival risks. Among the sources of contamination, irrigation and other agricultural activities exert direct and indirect effects on the rates and compositions of groundwater recharge and aquifer biogeochemistry (Amy et al., 1993; Böhlke, 2002; Fujita et al., 1996; Wilson et al., 1995).

In the arid and semi-arid regions of northwestern China, groundwater is the most important water source. In recent years, the use of groundwater for the area's water supply has been limited by increased contamination of the aquifers (Guo and Wang, 2005). Thus, groundwater safety and quality management has become increasingly important for sustainable development of these regions (Guo and Wang, 2004; Hua et al., 2010). Hydrogeological and geochemical studies provide essential data for sound scientific groundwater management.

Groundwater quality depends not only on natural factors (such as aquifer lithology, groundwater velocity, quality of recharge waters, and interaction with other types of water or aquifers), but also on human activities. Human behavior can alter these fragile systems either by polluting them or by modifying the hydrological cycle to such an extent that use of the groundwater becomes restricted. In particular, irrigation events accelerate groundwater quality change toward salinization in arid and semi-arid regions. Hutmacher et al. (1996) found that higher groundwater salinities (>20 dS/m) result in increased salinization of soils deeper in the profile, compared to treatments with less saline groundwater. Restricted use of shallow groundwater under such saline conditions limits the amount of salt accumulation in the upper part of the soil profile. Greater exploitation of the shallow groundwater in less saline soils, however, transports more salt to the upper part of the profile. Coupled with minimal leaching in the growing season, this results in greater salt accumulation in the soil profile (Hutmacher et al., 1996; King et al., 1995; Kruse et al., 1993; Northey et al., 2006). Excess salinity also reduces the osmotic activities of plants and therefore affects the absorption of nutrients and water (Prasad et al., 2001; Saleh et al., 1999).

In the present work, researchers undertook a study of the Jinghuiqu irrigation district, located in the Shaanxi Province of China (Figure 1A). This district has 2,200 years of irrigation history. The local groundwater is routinely used to irrigate more than two-thirds of the irrigation area, and about half of

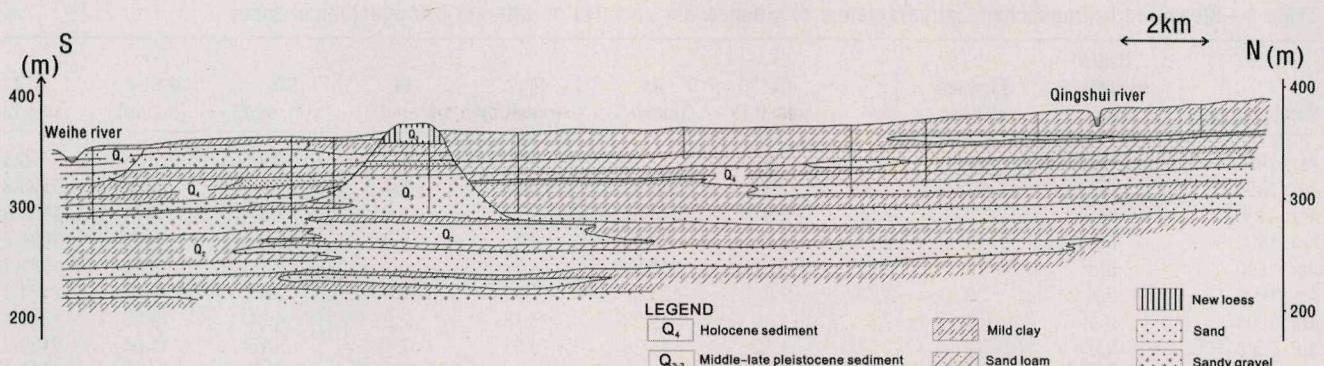


**Figure 1—(A)** Location map of the Jinghuiqu irrigation district (Shaanxi Province, China). **(B)** Layout of the groundwater sampling wells in 2009. Different colors and symbols (e.g., IA, IIA) represent hydrogeological conditions: IA—Jinghe river first terrace (extremely water-rich sub-district); IIA—Jinghe river second terrace (water-rich sub-district, south of the Yeyuhe and Qihe rivers); IIIA—Jinghe river third terrace (water-rich sub-district); IB—Weihe river first terrace (water-rich sub-district); IIB—Jinghe river second terrace (water-rich sub-district, north of the Qihe river); IIIB—Weihe river second terrace (water-rich sub-district); IIC—Jinghe river second terrace (water-rich sub-district, north of the Yeyuhe and Qihe rivers); IV—Loess Plateau (low-water sub-district).

the total irrigation water by volume is supplied by the groundwater. Nearly 80% of the water used by the domestic and industrial sectors is from the groundwater. Usually, the fields are irrigated two to three times a year with groundwater in the dry season, depending on the amount of precipitation, adding 18 to 24 cm of water each time. The remaining irrigation needs are satisfied by using the surface canal water. In 2007, a field survey showed that the groundwater had become seriously polluted and salinized. Because of these

findings, a field-based research project was initiated to determine the hydrochemical characteristics and the salinization processes of the groundwater aquifer, in order to develop wise and sustainable groundwater management policies.

Located in arid and semi-arid regions, the Jinghuiqu district has a permanent shortage of water resources for irrigation. Most of the existing research thus far focuses on the irrigation project system (Li, 1998; Liu, 2002); irrigation techniques (Gao, 2004); and water usage issues such as water optimization, efficient use



**Figure 2—Cross-section of the Jinghuiqu irrigation district and location of sampling wells and their various depths.**

of irrigation water, and optimal conjunctive use of surface and underground water (Li et al., 1999; Liu Xuan, 2005; Liu and Zhu, 2011; Zhao and Fei, 2006). Since 1990, because of the decreasing availability of canal water, the Jinghuiqu district has increased its amount of pumping from the aquifers in order to guarantee a constant amount of irrigation water, which lead to the groundwater table dropping significantly (Liu, 2010). However, the groundwater tables' rise and fall caused the water quality of the aquifer to change (Flores-López et al., 2011).

In this study, field-based investigations were carried out in order to investigate the chemistry of the groundwater aquifer, in addition to stable isotopes studies, in order to identify the controlling hydrogeochemical processes of the groundwater aquifer in Jinghuiqu irrigation district. The main research objectives were to: (1) study the groundwater quality changes over time and space, (2) analyze the geochemical formation processes of the shallow groundwater aquifer system; and (3) evaluate the risks of using the salinized groundwater for irrigation in the district, using three indices, namely the sodium adsorption ratio (SAR), the permeability index (PI) and the residual sodium carbonate (RSC).

**Regional Hydrogeology.** The Jinghuiqu irrigation district covers approximately 1,180 km<sup>2</sup> and is situated in the central part of Shaanxi province in China (Figure 1A). The district is bounded by the Loess plateau region in the north, the Weihe River in the south, the Shichuanhe River in the east and the Jinghe River in the west.

Based on the geological structure, the Jinghuiqu irrigation district belongs to the Weihe River graben, a Cenozoic fault-block basin filled predominantly with Tertiary fluvial and Aeolian sediments and Quaternary loess (Figure 1A); the thickness is more than 6,000 meters (Bellier et al., 1988). The upper part of the sedimentary filling of the Jinghuiqu irrigation district consists mainly of Quaternary fluvial deposits (Figure 2). Therefore, it constitutes an alluvial aquifer. The groundwater in this aquifer flows primarily from north to south. The aquifer can be roughly divided into eight hydrogeological units according to their lithological composition and permeability (IA, IIA, IIIA, IB, IIB, IIIB, IIC and IV; see Figure 1B), but over the years only six units can be irrigated (IA, IIA, IB, IIB, IIIB and IIC).

In Jinghuiqu, the depth of the shallow groundwater table was varying between 5 to 70 meters below the soil surface in 2009. Figure 1B shows the hydrogeological division of the shallow groundwater. The groundwater is recharged by vertically

infiltrating sources, such as precipitation and various irrigation waters, and laterally flowing surface waters from the Weihe, Shichuanhe, Qiyuhe and Jinghe rivers, as well as some irrigation return flow. Evapotranspiration, artificial abstraction, and lateral discharge to the rivers are the major discharge outlets of this groundwater aquifer. The confined groundwater depths are more than 100 meters below surface.

Climatologically, Jinghuiqu is located in a semi-arid region with a mean annual precipitation of approximately 533 mm; nearly 60% of the total annual rainfall is received between July and September. The mean annual temperature is 13.6°C, varying between a mean maximum of 42°C in July and a mean minimum of -24°C in January. The area's average annual potential evapotranspiration is 1,212 mm (Liu Y., 2010). In the irrigation region, winter wheat and maize are generally irrigated using water from the local groundwater between June and September. Surface water is usually used between November and May to maintain the ground water table. The total irrigation amount used is approximately 500 mm of water per year.

## Material and Methods

Groundwater samples were collected during three field trips—in April 1990, April and November 2008, and December 2009—for chemical and isotopic analyses. All water samples were taken from wells, 6 to 90 meters deep, used for domestic and agricultural water supply in different parts of the aquifer. The sampling locations are shown in Figure 1B. Groundwater samples were collected directly from the taps of the wells using a submersible pump, after 10 minutes of prior pumping. The sampled groundwater was collected over a period of three days during each of the testing periods, filtered through a 0.45-mm membrane, and collected in 250 mL polyethylene bottles for chemical analysis. Samples for cation analysis were preserved using ultra-pure HNO<sub>3</sub>.

All geochemical analyses were performed in the laboratory within four hours of sampling. The pH was measured using a potentiometric method. Cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) were analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Anions Cl<sup>-</sup> and SO<sup>2-</sup><sub>4</sub> were measured with ion chromatography. Bicarbonate (HCO<sub>3</sub><sup>-</sup>) was measured by acid-base titration. Cation and anion concentrations were determined with a detection limit of 0.001 mmol/L and an accuracy rate better than 2%.

Twelve samples from 2008 (eleven from groundwater and one from surface irrigation water) were selected for analysis, of the

**Table 1—Measured hydrogeochemical parameters of groundwater samples in different hydrogeological zones.**

Sampling date	Hydro-geological Unit	Samples number	pH	$\text{Ca}^{2+}$ (mmol/L)	$\text{Na}^+$ (mmol/L)	$\text{Mg}^{2+}$ (mmol/L)	$\text{Cl}^-$ (mmol/L)	$\text{SO}_4^{2-}$ (mmol/L)	$\text{HCO}_3^-$ (mmol/L)	TDS (mg/L)
Apr. 1990	IA	18	7.9	1.6	12.1	4.2	6.3	3.9	10	1656.3
Apr. 1990	IIA	47	7.88	2.2	14.8	6.4	8.4	5.1	10.2	1983.9
Apr. 1990	IB	2	7.58	2.9	13.3	2.2	3.5	2.3	8.7	1199.5
Apr. 1990	IIB	12	7.74	2.2	10.6	4.2	6.3	3.9	9.9	1684.7
Apr. 1990	IIIB	2	8.02	0.81	13.5	4.2	5.7	3.7	10.6	1641.4
Apr. 1990	IIC	7	7.88	2.0	23.3	7.8	12.8	7.8	12.7	2474.3
Apr. 2008	IA	3	7.6	1.39	12.03	7.73	7.92	4.94	12.25	1887.4
Apr. 2008	IIA	17	7.77	1.52	15.86	5.23	7.12	5.15	11.64	2129.3
Apr. 2008	IB	2	7.56	4.07	12.18	4.46	5.18	8.12	7.69	1733.6
Apr. 2008	IIB	9	7.68	1.54	19.75	5.65	8.55	6.62	12.20	1820.3
Apr. 2008	IIIB	3	7.97	1.03	15.99	4.63	6.37	4.73	11.33	1707.6
Apr. 2008	IIC	9	7.55	1.82	26.38	4.78	8.12	8.64	14.06	2899.0
Nov. 2008	IA	13	7.5	2.7	20.9	6.3	8.3	9.9	11.5	2397.8
Nov. 2008	IIA	16	7.71	1.8	19.6	5.6	8.8	7.9	10.5	2109.7
Nov. 2008	IB	2	7.6	3.8	17.2	3.5	4.9	9.1	9.4	2014.6
Nov. 2008	IIB	7	7.73	1.1	24.5	5.2	6.8	9.2	13	2332.6
Nov. 2008	IIIB	3	7.9	1.1	17.8	3.3	4.5	7.5	7.8	1715
Nov. 2008	IIC	6	7.69	2.3	31.5	6.1	13.4	12	12.3	3050
Dec. 2009	IA	13	7.47	2.5	19.6	7.1	9.1	9.2	9.5	2266.9
Dec. 2009	IIA	15	7.59	1.8	24.2	7.2	9.4	10	10.8	2476.9
Dec. 2009	IB	3	7.69	1.8	11.9	2.4	2.5	5.6	5.6	1223
Dec. 2009	IIB	8	7.65	1.3	28	6.4	8.1	10.3	12.5	2564.3
Dec. 2009	IIIB	3	7.85	1.0	18.2	4.1	5.2	6.3	9.2	1663.4
Dec. 2009	IIC	5	7.56	1.8	35.2	7.2	11.3	13.2	12.8	3188.3

$\delta^{18}\text{O}$  and  $\delta\text{D}$  values of  $\text{H}_2\text{O}$  and the  $\delta^{34}\text{S}$  values of  $\text{SO}_4^{2-}$ , at the State Key Laboratory of Environmental Geochemistry of the Institute of Geochemistry, Guiyang. Samples were prepared for  $^{18}\text{O}/^{16}\text{O}$  analysis by  $\text{CO}_2$  equilibration (Epstein and Meyeda, 1953) and for D/H analysis by zinc reduction (Coleman et al., 1982). Analyses were made using the ISOPREP-18 system, followed by isotope ratio mass spectrometry (VG-SIRA II) and calibrated against the NBS-19 standard following Coplen (1988). Oxygen and hydrogen isotope analyses are reported in the usual  $\delta$  notation as permil deviations from the SMOW reference standards (Fontes, 1976). The analytical precision was  $\pm 0.1\%$  for  $\delta^{18}\text{O}$  and  $\pm 2\%$  for  $\delta\text{D}$ .

In the laboratory tests at Guiyang, the sulfate was eluted from the column and precipitated as  $\text{BaSO}_4$  by adding a  $\text{BaCl}_2$  solution. The filtered, washed and dried  $\text{BaSO}_4$  was converted to sulfur dioxide ( $\text{SO}_2$ ) in an elemental analyzer and swept with a helium stream into an isotope ratio mass spectrometer (the VG Prism II) for isotope ratio determinations. For oxygen isotope analyses on  $\text{SO}_4^{2-}$ ,  $\text{BaSO}_4$ -oxygen was converted to  $\text{CO}$  at  $1450^\circ\text{C}$  in a pyrolysis reactor (Finnigan TC/EA). The resultant gas was subsequently swept with a helium stream into a mass spectrometer (Finnigan MAT delta plus XL) for isotope ratio determinations in continuous-flow mode (CF-IRMS). Stable isotope ratios are reported in the usual  $\delta$  notation in permil with respect to the international standards: V-CDT for sulfur isotope measurements and V-SMOW for oxygen isotope measurements (Shanley et al., 2005). Precision (standard deviation on replicate analyses) averaged  $\pm 0.3\%$  for the  $\delta^{34}\text{S}-\text{SO}_4$  values.

## Results and Discussion

**Hydrochemical Characteristics.** Chemical compositions of the groundwater samples obtained in April 1990, April and

November 2008, and December 2009 are summarized in Table 1. The ion concentrations were similar in 2008 and 2009, so the 1990 and 2009 values are mainly presented here.

As shown in Table 1, the total dissolved solids (TDS) for the collected water samples ranged from 1,003 to 3,389.6 mg  $\text{L}^{-1}$  in 1990. Nineteen years, however, later the TDS ranged from 805.8 to 5,134.2 mg  $\text{L}^{-1}$ . The changes of the major cations and anions over the 19-year period are shown in Figure 3. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations decreased slightly. The  $\text{Na}^+$  cation concentrations increased from  $13.12 \text{ mmol L}^{-1}$  to  $21.45 \text{ mmol L}^{-1}$  over the years. The major  $\text{SO}_4^{2-}$  anion values increased from an average value of  $4.8 \text{ mmol L}^{-1}$  in 1990 to  $9.8 \text{ mmol L}^{-1}$  in 2009. The  $\text{HCO}_3^-$  concentrations increased slightly. The  $\text{Cl}^-$  concentration range expanded from  $2.6 - 21.2 \text{ mmol L}^{-1}$  to  $1.0 - 24.2 \text{ mmol L}^{-1}$  (Figure 3).

Table 1 also shows that the pH value decreased in all hydrogeological units of the irrigation district except the IB unit. The  $\text{Ca}^{2+}$  concentrations slightly decreased in the IIA, IB, IIB and IIC units. However,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  concentrations increased dramatically from 1990 to 2009, especially in the IIA, IIB and IIC zones.  $\text{Mg}^{2+}$  concentrations increased in the IA, IIA, IB and IIB units. The  $\text{Cl}^-$  and  $\text{HCO}_3^-$  concentrations did not show a clear trend.

Throughout the district, among the major cation milliequivalent percentages in 1990, Na and K predominated, representing 49% of the sum of cations.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  represented 15% and 36% of the total cations respectively. Among the major anions,  $\text{HCO}_3^-$  dominated the spectrum (at an average of 40% of the anions), whereas  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  represented 33% and 27% of the sum of the anions, respectively. In 2009, the major cations Na and K predominated, representing up to 58% of the sum of the cations. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  represented 9% and 33% of the total

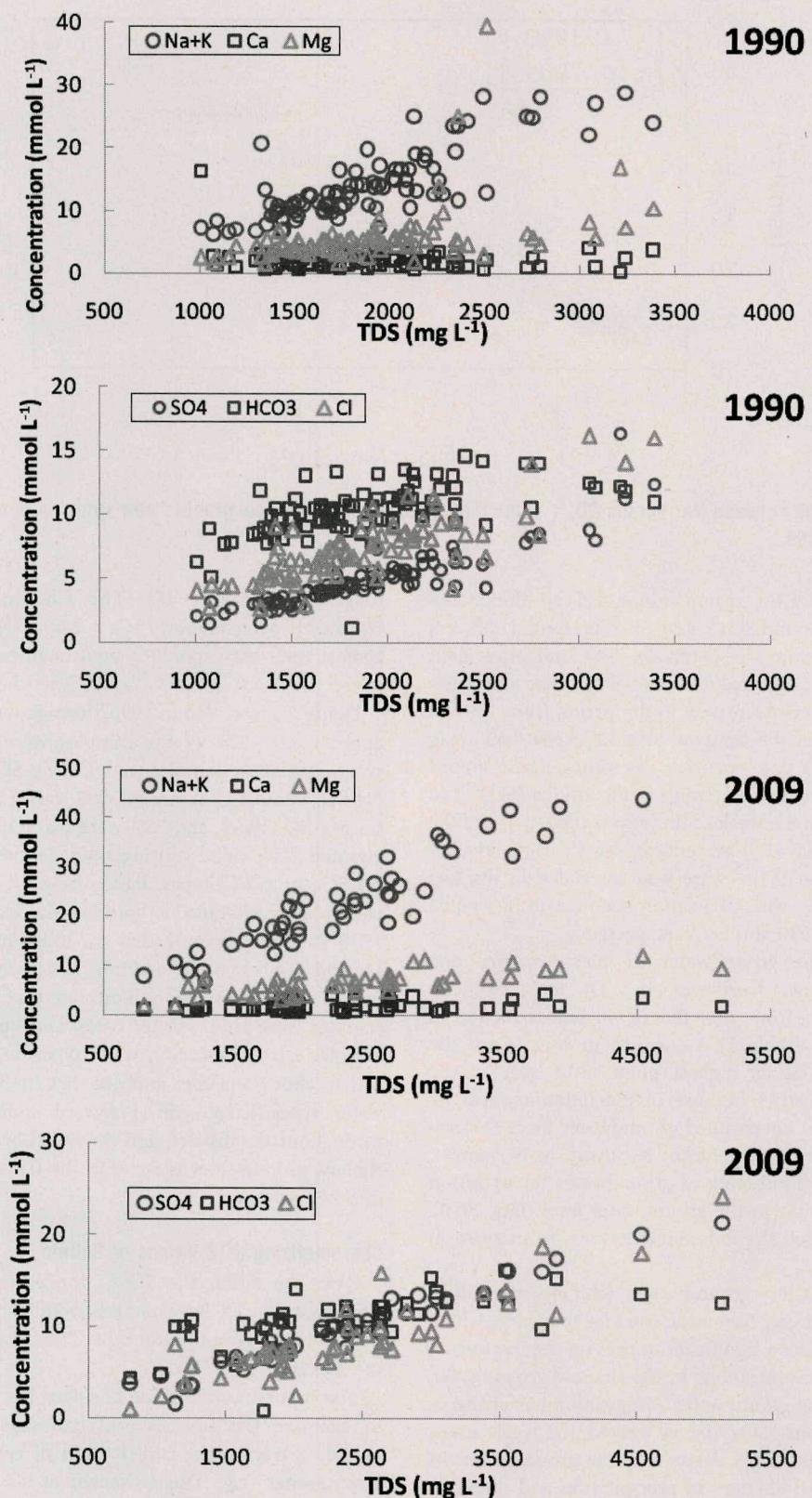
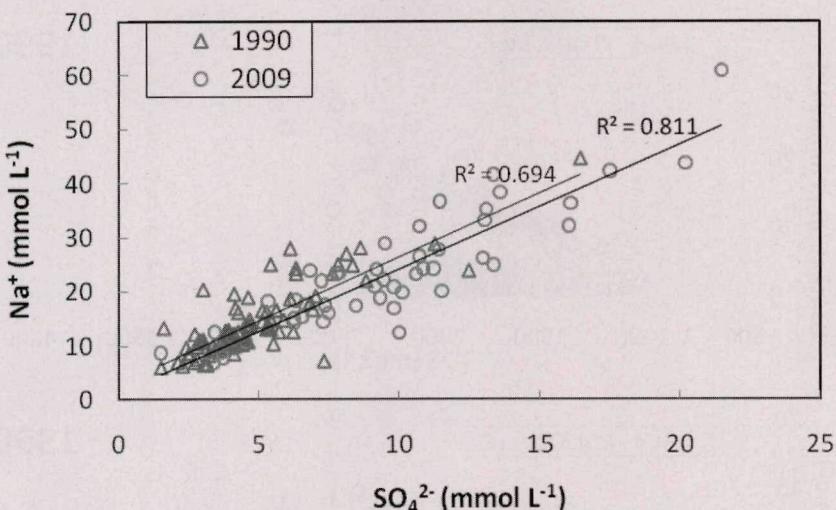


Figure 3—Relationships between TDS and cation and anion concentrations in the tested groundwater samples obtained from the Jinghuiqu irrigation district in 1990 (top) and 2009 (bottom).



**Figure 4—Relationships between  $\text{Na}^+$  versus  $\text{SO}_4^{2-}$  values measured from the shallow groundwater samples of the Jinghuiqu irrigation district in 1990 and 2009.**

cations, respectively. Of the major anions,  $\text{HCO}_3^-$  dominated with an average of 29%, and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  represented 50% and 21% of the total anions, respectively. The milliequivalent percentage of ions showed that  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  had obviously increased, and the others decreased, in the period from 1990 to 2009. In 1990, most of the samples' alkaline earths had weak acidic anions ( $\text{HCO}_3^-$ ) that exceeded the strong acidic anions ( $\text{SO}_4^{2-}$ ). In 2009, however, the strong acidic anions ( $\text{SO}_4^{2-}$ ) of most samples exceeded the weak acidic anions ( $\text{HCO}_3^-$ ), and the cation alkali metals ( $\text{Na}^+ + \text{K}^+$ ) percentage also clearly increased.

Statistically,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  were well correlated in the two time periods (Figure 4), with correlation coefficients ( $R^2$ ) equal to 0.694 and 0.81 in 1990 and 2009, respectively.

A comparison of the groundwater samples in April and November of 2008 is also worthy of note. The ion concentrations in April 2008 were lower than that of November 2008 in all hydrogeological units (Table 1). Generally, in early April the groundwater table is at its highest point of the year in the Jinghuiqu irrigation district because of precipitation recharge and decreased demand for pumped groundwater from December to April each year. However, from late April to November, each year the extensive pumping of groundwater for irrigation has led to a sharp decline in the groundwater level (Liu, 2010). This process also caused the ion concentrations to increase in November.

Since 1990, the local deep groundwaters, with elevated sulfate and sodium concentrations, have been used for irrigation, which has the potential to make a significant impact on the increase of sulfate and sodium concentrations in the shallow groundwater. Due to the fact that the groundwater composition has changed, the strong acidic anions ( $\text{SO}_4^{2-}$ ) now exceed the weak acidic anions ( $\text{HCO}_3^-$ ), causing a pH decrease in the groundwater. At the same time, seasonal changes in precipitation and pumping cause the water tables to rise and fall seasonally. This resulted in a small change in the water quality within a year.

**Groundwater Chemical Types.** To classify the groundwater and identify the hydrochemical processes, a Chadha diagram (Chadha, 1999) was used. This diagram is a modified version of the Piper diagram (Piper, 1944) and the expanded Durov

diagram (Durov, 1948). The Chadha diagram plots the equivalent percentages of  $(\text{Ca} + \text{Mg}) - (\text{Na} + \text{K})$  of the samples against their corresponding equivalent percentages in terms of  $(\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{SO}_4^{2-} + \text{Cl}^-)$ , as shown in Figure 5.

Figure 5 shows that in 1990, throughout the irrigation district, approximately 2% of the samples were Ca-Mg-HCO<sub>3</sub> water types, 70% of the samples were Ca-Mg-SO<sub>4</sub> types, and 28% were Na-SO<sub>4</sub> and Na-Cl types. In 2009, only 22% of the samples were Ca-Mg-SO<sub>4</sub> types, and 78% were Na-SO<sub>4</sub> and Na-Cl types. The elevated TDS values during both periods mostly reflected the Na-SO<sub>4</sub> or Na-Cl types. Particularly, Na-SO<sub>4</sub> and Na-Cl types were mainly identified in parts of the IA, IIA and IIC units in 1990. In 2009, however, they expanded to the IB, IIB, IIIB, IIC, IA and IIA units. In addition, a survey from the Jinghuiqu irrigation administration indicated that in 1982, 82% of the samples were HCO<sub>3</sub> water types, and only 18% and 1% of the samples were Cl and SO<sub>4</sub> water types, respectively.

The above analyses indicate that in Jinghuiqu, the groundwater types have evolved toward sodic salinity ( $\text{Na}-\text{SO}_4^{2-}$ ) throughout the district, and the speed of the salinization of the shallow groundwater is faster in the IIB, IIIB and IA parts than in other sectors.

#### Characterizing $\delta^{34}\text{S}$ Values of Sulfate

Over the years, the  $\text{SO}_4^{2-}$  concentrations throughout the Jinghuiqu district have increased and have gradually come to dominate the groundwater type. Thus, it is necessary to identify the source of  $\text{SO}_4^{2-}$ .

The isotopic composition of sulfate has been successfully used to examine the sources and pathways of the sulfur cycle, including tracing the contribution of anthropogenic sulfate to groundwater (e.g., Dugan Kaown et al., 2009; Mitchell et al., 1998; Van Donkelaar et al., 1995). Typical  $\delta^{34}\text{S}$  values range from  $-15\text{\textperthousand}$  to  $+14\text{\textperthousand}$  for mineral sulfate, from  $-34\text{\textperthousand}$  to  $+7\text{\textperthousand}$  for sulfate derived from the oxidation of reduced sulfur minerals, and from 0 to  $+6\text{\textperthousand}$  for sulfate in atmospheric deposition in industrialized countries (Krouse and Mayer, 2000; Mayer, 2005; Rock and Mayer, 2002).

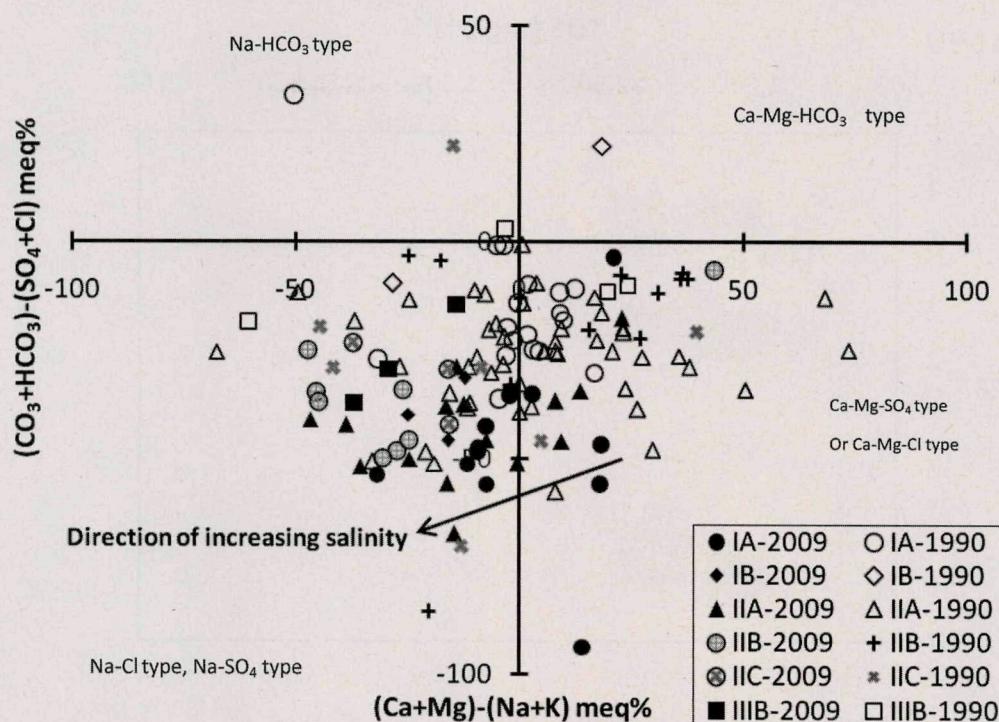


Figure 5—A Chadha diagram for the Jinghuiqu irrigation area in 1990 and 2009.

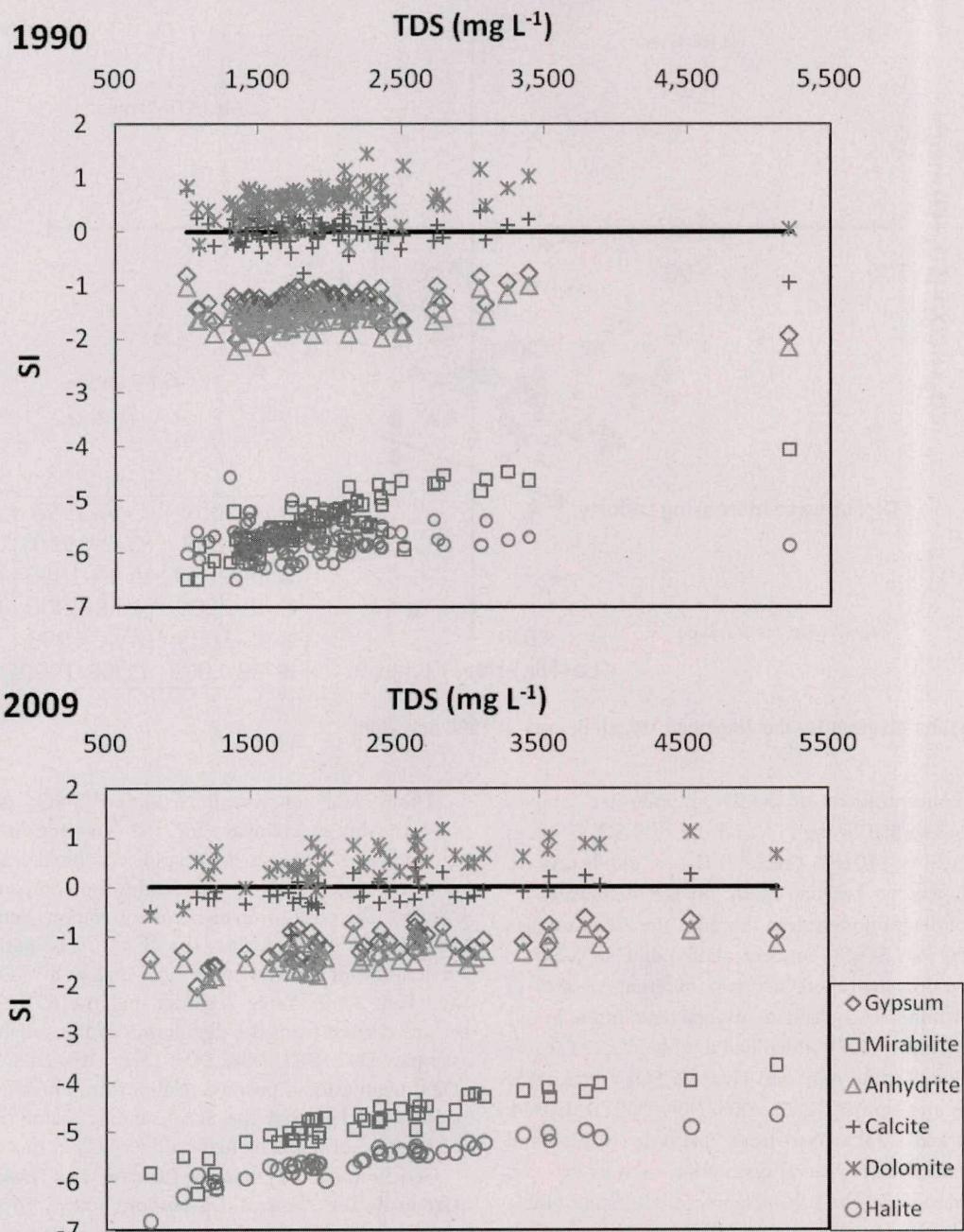
The sulfate concentrations of the 11 groundwater samples varied from 167.8 to 886.76 mg L<sup>-1</sup>, and the  $\delta^{34}\text{S-SO}_4^{2-}$  values ranged from +5.27 to +10.69‰ (Table 2) (Liu et al., in review). Although there was no baseline study on the natural SO<sub>4</sub><sup>2-</sup> isotope values of the groundwater in this area, the literature (Ma and Fan, 2005) on SO<sub>4</sub><sup>2-</sup> concentrations and  $\delta^{34}\text{S-SO}_4^{2-}$  relationship revealed that there are two different sources of oxidation: sulfur minerals and sulfate mineral dissolution. In our study, only one sample (D07), which had a value of 5.27‰, came from the oxidation of sulfur minerals. The  $\delta^{34}\text{S-SO}_4^{2-}$  values of the other 9 groundwater samples (D02, D03, D08, D09, D11, D14, D18, D20, D22 and D23) ranged from 7.84‰ to 10.69‰ and were derived from sulfate mineral dissolution such as gypsum, anhydrite and mirabilite. The sulfate source is consistent (Table 2) throughout different hydrogeological units.

The sulfate concentrations and  $\delta^{34}\text{S-SO}_4^{2-}$  values can also explain the mechanism for the dissolution of sulfate in groundwater, because no amount of biological fractionation occurred (according to this study's microorganism measured results). The positive or negative correlations between  $\delta^{34}\text{S-SO}_4^{2-}$  and SO<sub>4</sub><sup>2-</sup> indicate that the SO<sub>4</sub><sup>2-</sup> was derived from the dissolution of minerals with high or low  $\delta^{34}\text{S-SO}_4^{2-}$  values (Ma and Fan, 2005). Table 2 shows that the  $\delta^{34}\text{S-SO}_4^{2-}$  and SO<sub>4</sub><sup>2-</sup> values derived from the dissolution of the sulfate minerals (in samples D02, D03, D08, D09, D11, D14, D18, D20, D22 and D23) manifested a positive relationship. Therefore, the conclusion is reached that the SO<sub>4</sub><sup>2-</sup> anions mainly came from the dissolution of minerals high in  $\delta^{34}\text{S-SO}_4^{2-}$  in the study area.

**Geochemical Formation Process and Evolution of the Groundwater. Mineral Dissolution Action.** To investigate the thermodynamic controls on water composition, an equilibrium

Table 2—Isootope values and calculations of the surface water mixing ratio (%) of the groundwater.

Well	$\delta\text{D}/10^{-3}$	$\delta^{18}\text{O}/10^{-3}$	$\delta^{34}\text{S-SO}_4/10^{-3}$	Surface water mixing ratio (%)	Depth of well (m)	Hydrogeological unit-geological zone
D-02	-66.3	-8	9.43	14	70	IIA
D-03	-61	-7.07	10.15	60.5	60	IA
D-07	-62.6	-7.43	5.27	42.5	50	IIA
D-08	-70.7	-8.28	7.84	0	90	IIA
D-09	-64.3	-7.44	9.69	42	36	IIA
D-11	-62.9	-7.65	9.43	31.5	60	IIA
D-14	-61.8	-7.15	9.7	56.5	18	IIC
D-18	-63.6	-7.33	8.6	47.5	30	IIB
D-20	-67.5	-7.99	10.3	14.5	40	IIA
D-22	-62.1	-7.36	9.11	46	40	IIA
D-23	-65.9	-7.76	10.69	26	70	IIIB



**Figure 6**—The log SI for gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), halite ( $\text{NaCl}$ ), calcite ( $\text{CaCO}_3$ ), and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) versus the TDS of the groundwater in 1990 (top) and 2009 (bottom).

speciation calculation was conducted using the PHREEQC program (Parkhurst and Appelo, 1999). These calculations provided saturation indices (SI) of minerals that might be reacting in the system. The SI of a particular mineral can be defined as:

$$SI = \log(IAP/K_t) \quad (1)$$

where  $IAP$  is the ion activity product of the mineral–water reaction, and  $K_t$  is the thermodynamic equilibrium constant, adjusted to the temperature of the given sample.

Figure 6 presents the saturation indices (SI) of the possible reacting soluble minerals in 1990 and 2009. It can be seen that all

the samples of the groundwater studied were undersaturated with respect to anhydrite, gypsum, mirabilite and halite, suggesting dissolution. This dissolution indicates that these minerals influenced the chemical composition of the groundwater. Calcite was saturated in most wells in both sample periods. Dolomite was saturated in 2009, indicating that the carbonate minerals varied with precipitation. Although all the halite SIs were unsaturated in both 1990 and 2009, due to  $\text{Cl}^-$  concentration, the values increased slightly over the years, suggesting that mineral phases are minor or absent in the host rocks.

**Cations Exchanged.** The cation-exchange direction depends on the minerals that are encountered along the vertical (from

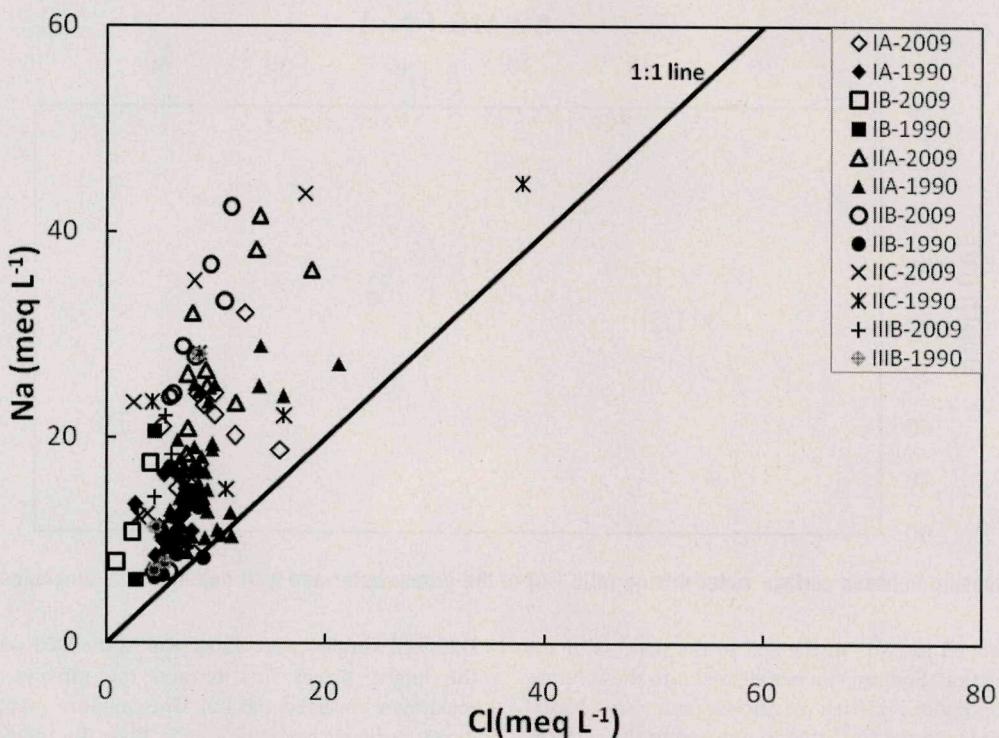


Figure 7—Ion concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the groundwater samples in 1990 and 2009.

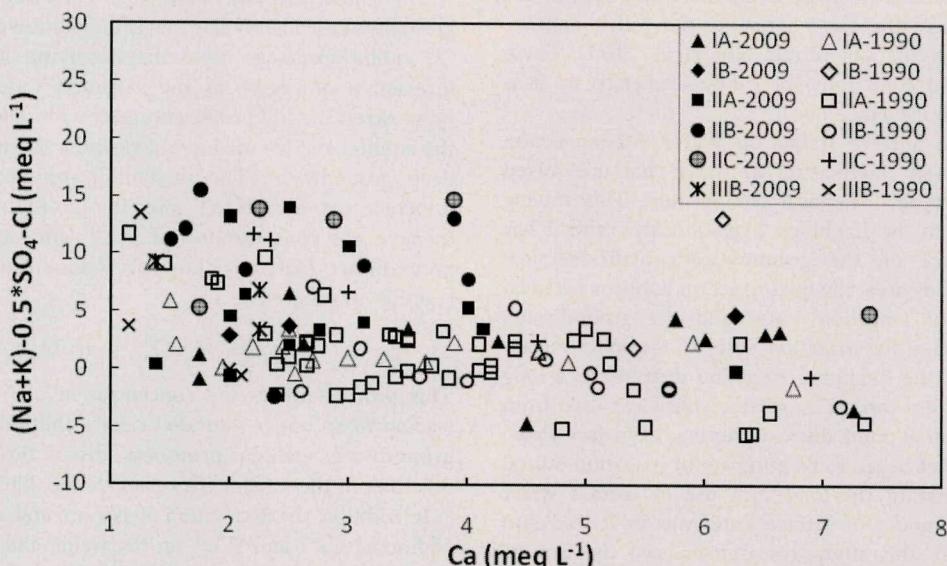
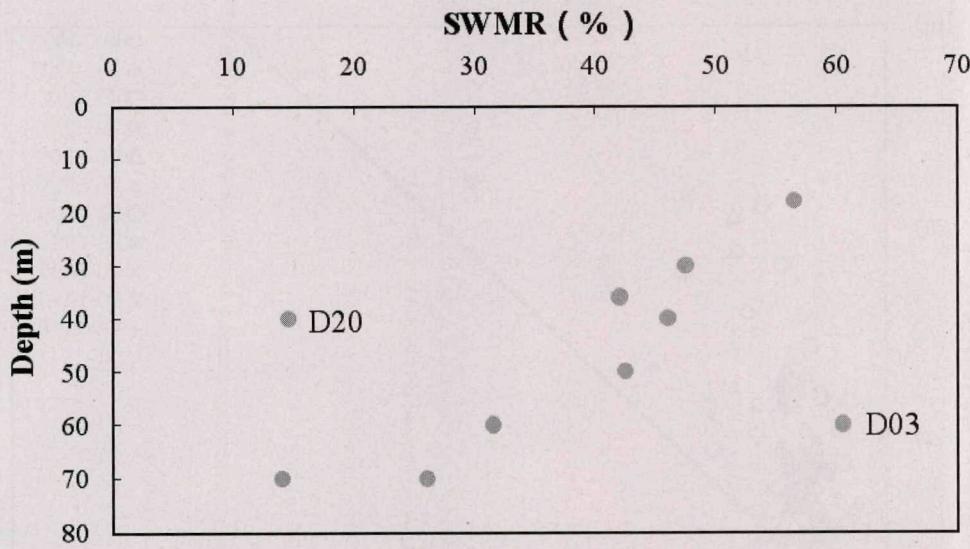


Figure 8—Ion concentrations of  $\text{Ca}^{2+}$  and  $(\text{Na}^++\text{K}^+)-0.5\text{SO}_4^{2-}-\text{Cl}^-$  in the groundwater samples in 1990 and 2009.

irrigation water and rainfall) and horizontal flow paths, before the water enters the unit in which the exchange occurs. Dissolved chloride can be used as a conventional reference parameter because in many halite-free environments, few processes other than mixing can affect its concentration (Hanor, 1987). The evolution of the  $\text{Na}^++\text{K}^+$  content with respect to the  $\text{Cl}^-$  content (Figure 7) shows that, for the majority of the investigated samples, there was an excess of sodium content. From 1990 to 2009, the  $\text{Na}^+$  concentrations increased in large

areas in the IIA, IIB, and IIC units, indicating an external source of sodium.

The changes of  $\text{Ca}^{2+}$  contents versus  $(\text{Na}^++\text{K}^+)-0.5\text{SO}_4^{2-}-\text{Cl}^-$  (Figure 8) show that, except for the dissolution of mirabilite and some halite minerals, the  $\text{Na}^+$  contents still increased from 1990 to 2009. This indicates a source of cation exchange over the years in the whole area, especially in the IIA, IIB and IIC units. The  $\text{Ca}^{2+}$  contents also tended to drop in these areas, although some of the  $\text{Ca}^{2+}$  concentration may have come from the dissolution of gypsum and anhydrite. The  $\text{Ca}^{2+}$  cation in the



**Figure 9—Relationship between surface water mixing ratio (%) of the groundwater and well depths in the Jinghuiqu area.**

solution is exchanged for  $\text{Na}^+$  in the soil in the process of the water-rock interaction. Sodium can be released into the solution during the weathering of  $\text{Na}^+$ -rich plagioclase, and also released by cation exchange with the  $\text{Ca}^{2+}$  that is attached to the surfaces of newly formed clay minerals (Iwatsuki and Yoshida, 1999). Based on the mineral analyses in the IIB unit, there is an abundance of plagioclase (19%) and clay minerals (14%) in the Jinghuiqu area, where the clay content of the soil is approximately 22.2% along the soil profile (Liu et al., 2011). These values provide good conditions for cation exchange, so it is assumed that cation exchange occurred.

**Mixing with the Surface Irrigation Water.** Mixing action refers to the different ingredients in water that are mixed together, forming a new chemical composition. This mixing action is common in the Jinghuiqu irrigation area, and it has significant influence on the groundwater's hydrochemical evolution. In the study area, the mixing action happens between different sources of irrigation water and the groundwater, through infiltrations of the irrigation water to the water table.

As noted earlier, the Jinghuiqu irrigation district has a long irrigation history. Until the 1970s, surface water was used from the Jinghe River. At that point, due to a shortage of surface water, the local groundwater began to be pumped for irrigation during dry seasons. Because of the long-term use of surface water irrigation, a large amount of surface water was infiltrated into the groundwater. In this study, researchers used the isotope value of  $\delta^{18}\text{O}$  to calculate the surface water mixing ratio (%) (SWMR) of the groundwater (Ma et al., 2007) as follows:

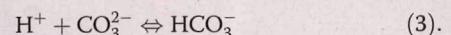
$$\text{SWMR} = \frac{\delta^{18}\text{O}_{\text{groundwater}} - \delta^{18}\text{O}_{\text{measured}}}{\delta^{18}\text{O}_{\text{groundwater}} - \delta^{18}\text{O}_{\text{surface water}}} \times 100\% \quad (2),$$

where SWMR is surface water mixing ratio (%) of the groundwater, and  $\delta^{18}\text{O}_{\text{groundwater}}$ ,  $\delta^{18}\text{O}_{\text{measured}}$ , and  $\delta^{18}\text{O}_{\text{surface water}}$  are  $\delta^{18}\text{O}$  values of the deep groundwater well, measured well, and surface irrigation water, respectively.

Table 2 lists the calculated results, showing that the surface water mixing ratio (%) in the groundwater varied dramatically from 14% to 60.5%. When the well is deeper, the mixing proportion is generally smaller (Figure 9). However, the D03 and

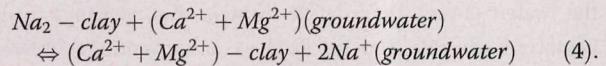
D20 well samples were abnormal. In the D03 well, which is near the Jinghe River's first terrace, the mixture ratio is at the maximum observed (60.5%). This mixture may be impacted by direct recharge from the Jinghe River, in addition to irrigation. The D20 well, located in Jinghe River's second terrace, may be influenced more by hydrogeological conditions and other factors.

The above analyses show that chemical evolution of the groundwater is mainly due to: (1) dissolution of sulfate minerals; (2) cation exchange reactions occurring in the water-rock interaction processes, as the irrigation water and rain water move down the soil profile and react with the horizontal flow in the aquifer; and (3) mixing of irrigation waters with surface and deep groundwater. The dissolution products of the sulfate minerals are introduced into the groundwater where they increase the concentration of  $\text{SO}_4^{2-}$  and decrease pH of the groundwater (Table 1). Low pH values caused the following reaction to proceed:

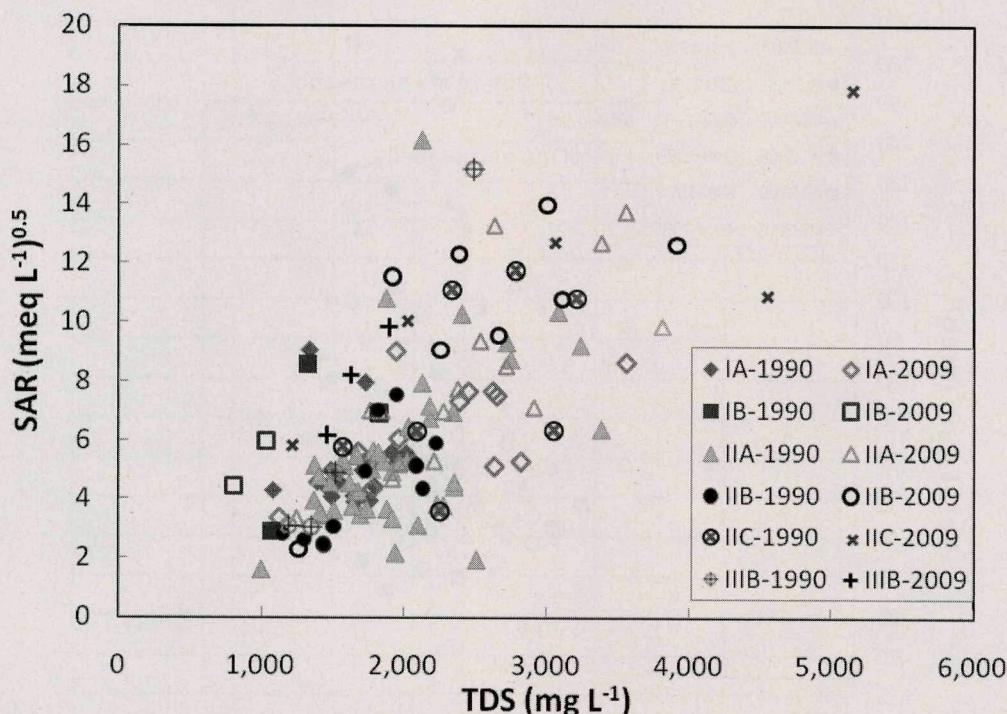


This process causes the concentration of  $\text{CO}_3^{2-}$  to decrease, leading to an under-saturated calcite and dolomite state in the groundwater, which promotes dissolution of calcite and dolomite in the aquifer (Guo and Wang, 2005).

In addition, the dissolution of gypsum and anhydrite produces additional  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the water, and causes supersaturated calcite in the groundwater. Furthermore, the ion exchange processes also take place. Thus, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the groundwater exchange with previously absorbed  $\text{Na}^+$  on the surface of clay minerals in the aquifer matrix, as shown below:



This reaction would decrease the concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and increase that of  $\text{Na}^+$  in groundwater (Hidalgo and Cruz-Sanjulian, 2001). But in a slightly stagnant environment,  $\text{Ca}^{2+}$  instead of  $\text{Mg}^{2+}$  would have firstly been exchanged with  $\text{Na}^+$ , which was absorbed on the surface of clay minerals (Shen et al., 1993). In the groundwaters of the Jinghuiqu district, ion



**Figure 10—TDS and SAR in the groundwater samples in 1990 and 2009.**

exchange mainly made the concentrations of  $\text{Na}^+$  (in the whole district) and  $\text{Mg}^{2+}$  (in the IA, IIA, IB and IIB areas) higher. So over the years, the reaction products could have influenced and controlled the mobile dissociation equilibrium of calcite and dolomite. However, the mixing of surface irrigated water could make the minerals dissolve again.

**Suitability of Groundwater for Irrigation.** In order to evaluate the risks of groundwater irrigation on soil and plant quality, this study further examined the groundwater quality changes from 1990 to 2009, using three indices: the sodium adsorption ratio (SAR), the permeability index (PI), and residual sodium carbonate (RSC).

The sodium adsorption ratio (SAR) is often used by soil scientists as a measure of the sodium hazard of irrigation water (Richards, 1954). The SAR is calculated as follows:

$$\text{SAR} = \frac{\text{N}_a^+}{\sqrt{\frac{(\text{C}_a^{2+} + \text{M}_g^{2+})}{2}}} \quad (5),$$

where the parentheses denote concentrations of the ions in  $\text{mEq L}^{-1}$ .

When waters with high sodium concentrations relative to the concentrations of magnesium and calcium are used for irrigation, they tend to alter the properties of the soil, thus affecting its agricultural functionality. Problems with soil structure arise when  $\text{Na}^+$  forms approximately 15% of the exchangeable cations, and the ionic strength is less than 0.015 (Appelo and Postma, 2005). High concentrations of sodium ions in water affect the permeability of soil, causing infiltration problems. This is due to the fact that sodium is adsorbed on the soil clays, causing the dispersion of soil particles. This dispersion results in the breakdown of soil aggregates. The soil becomes hard and compact

when dry, and it reduces the infiltration rates of water and air in the soil. The problem is also related to several other factors, such as salinity rate, type of soil, and crop tolerance.

The SAR values of the groundwater in the entire Jinghuiqu irrigation area ranged from  $1.64$  to  $16.17$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$  in 1990 and  $2.3$  to  $17.9$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$  in 2009, with average values of  $6.5$  and  $8.2$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$  in 1990 and 2009, respectively (Figure 10).

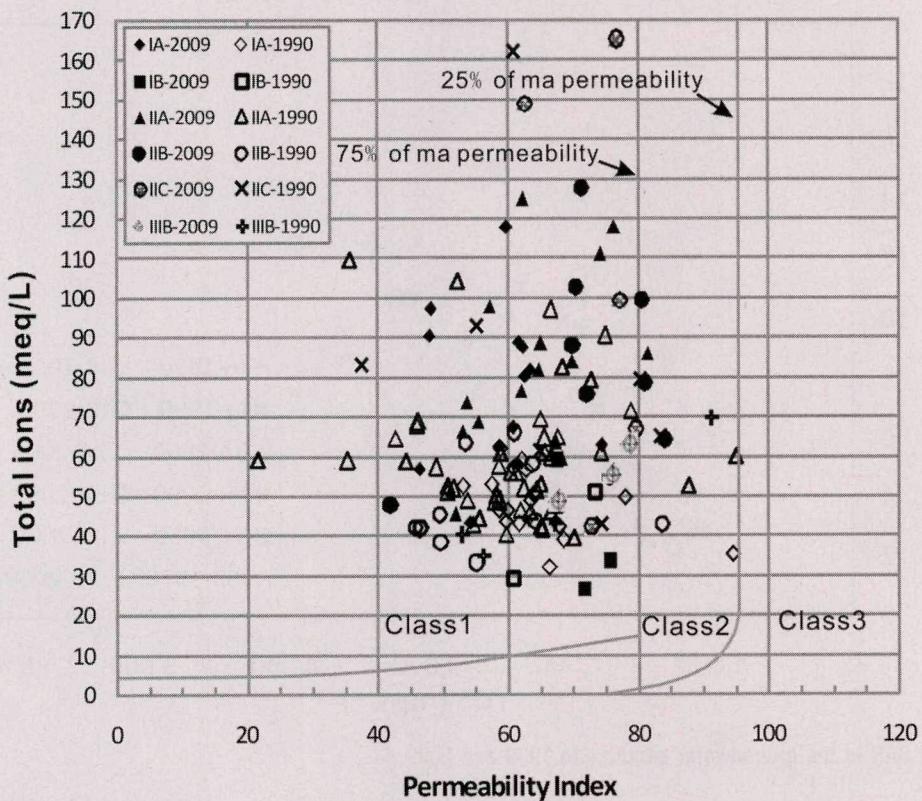
Based on irrigation water standards (Song et al., 2000), if the SAR value of the groundwater is between  $8$  and  $18$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$ , the groundwater quality must be appropriately controlled. If it is more than  $18$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$ , the groundwater can no longer be used for irrigation. In 1990, the SAR values of the Jinghuiqu groundwater samples were less than  $8$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$  accounting for 84% of the total samples; about 16% of the samples had SAR values varying between  $8$  and  $18$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$ . In 2009, however, about 48% of the samples had SAR values between  $8$  and  $18$  ( $\text{mEq L}^{-1}$ ) $^{0.5}$ . In the spatial distribution, the SAR increased greatly in the IIB, IIA, IIC, IIIB and IA units. In 1990, the groundwater had elevated SAR values only in parts of the IIA and IIC units. In 2009, however, elevated SAR values expanded to the IIB, IIC, IIIB, IA and IIA units of the irrigation district.

The permeability index (PI) of a water sample is calculated using Eq. (6), and it gives an indication of the probable effects of the water on soil permeability when used for irrigation:

$$\text{PI} = \frac{(\text{Na}^+ + \sqrt{\text{HCO}_3^-})}{(\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})} \times 100\% \quad (6),$$

where the concentrations are in  $\text{mEq/L}$ .

The calculated results are plotted on a Doneen's chart (Domenico and Schwartz, 1990), as shown in Figure 11. In terms of the permeability indices, Class 1 waters are the best water types for irrigation purposes. Class 2 waters are of intermediate quality and may be used for irrigation with some



**Figure 11—A Doneen's chart for the study area.**

caution, and Class 3 waters are of unacceptable quality for irrigation (Yidana, 2010). It is obvious from Figure 11 that only a small number of samples from the IIA and IIB units fell within Class 2 parameters, but the PI values are obviously increasing in the IA, IIA, IIB, IIIB and IIC units. The average PI values changed from 61.1 to 66.2 over the entire irrigation area.

Residual sodium carbonate (RSC), as defined by Eq. (7), is another index used to assess the quality of water for irrigation purposes. The RSC measures the excess of carbonate and bicarbonate over the sum of the concentration of magnesium and calcium:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Mg + Ca) \quad (7)$$

where the concentrations are in mEq/L.

Waters with high RSC have deleterious effects on plant development and are not suitable for irrigation. Waters with an RSC < 1.25 are of excellent irrigation quality and can be used for the irrigation of almost all crops without the risks associated with residual sodium carbonate. Waters with RSC values higher than 2.5 are not acceptable for irrigation. If the RSC is between 1.25 and 2.5, the water is of an acceptable quality for irrigation (Yidana 2010). Table 3 summarizes the irrigation quality of the major groundwater groups established in the Jinghuiqu irrigation district. Based on the RSC, from 1990 to 2009, the percentage of excellent irrigation quality water increased throughout the whole irrigation district. This is due to the fact that  $HCO_3^-$  concentrations are dropping and the groundwater is gradually becoming more acidic.

**Table 3—A summary of the RSC values for the groundwater in 1990 and 2009 (mEq L<sup>-1</sup>).**

Year	Hydrogeological unit	Mean	Minimum	Maximum	Excellent (%)	Acceptable (%)	Poor (%)
1990	IA	-1.77	-6.19	7.42	94	0	6
	IIA	-1.4	-2.9	0.1	92	2	6
	IB	-6.93	-40.03	6.33	100	0	0
	IIB	-3.02	-9.6	7.37	83	0	17
	IIIB	-6.89	-22.11	4.03	75	0	25
	IIC	0.46	-3.5	7.37	57	0	43
2009	IA	-9.3	-17.1	-2.9	100	0	0
	IIA	-6.8	-17.1	0.82	100	0	0
	IB	-2.56	-4.7	-1.43	100	0	0
	IIB	-2.4	-6.3	3.2	75	12.5	12.5
	IIIB	-0.75	-3.66	0.89	100	0	0
	IIC	-4.7	-17.77	3.82	60	20	20

The above analyses indicate that the groundwater in the entire irrigation district is trending toward salinity. This has already impacted the permeability of soil for irrigation, especially in the IA, IIA, IIB, IIIB and IIC units. It is apparent that the salinity issue is the deciding factor for the groundwater's suitability for irrigation. Long-term irrigation using this groundwater will likely lead to the accumulation of large quantities of ions in the soils and groundwater, which will lead to soil salinization and harm to plants.

## Conclusions

In the Jinghuiqu irrigation district, the Na, K, and  $\text{SO}_4^{2-}$  concentration values increased dramatically from 1990 to 2009, and the affected area is expanding. In less than 30 years (1982–2009), the hydrochemical type of groundwater changed from an  $\text{HCO}_3^-$  type into an  $\text{SO}_4^{2-}$  type throughout the whole area. The analysis indicates that the initial higher  $\text{SO}_4^{2-}$  concentration came from the dissolution of high  $\delta^{34}\text{S}-\text{SO}_4^{2-}$  minerals, and the  $\text{Na}^+$  concentration came from mineral dissolution and cation exchange, both in the water-rock interaction during the irrigation water infiltration, and in the groundwater horizontal flow within the aquifer.

An additional comparison was made between seasonal groundwater samples in April and in November 2008. The ion concentrations measured in April were lower than those measured in November in all hydrogeological units, because of both precipitation recharge and a reduced amount of irrigation pumping. However, flood irrigation events have been hastening the salinization of the shallow groundwater. During the past 20 years, the mixture of local deep irrigation groundwater sources with elevated sulfate and sodium concentrations has made a significant influence on the evolution of the shallow groundwater (Liu et al., in review). The water types evolved towards an  $\text{Na}-\text{SO}_4^{2-}$  type throughout the whole irrigation district, especially in the middle and eastern sections of the district (the IIA, IIB, IIC and IIIB units; see Figure 1B), and the groundwater is gradually becoming acidic.

The suitability assessment of the groundwater in 2009 indicates that a large part of the shallow groundwater used for irrigation, with elevated SAR (in the IIB, IIC, IIIB, IA and IIA units of the irrigation area), has affected the soil permeability. Most of the groundwater cannot be used for the domestic water supply or long term irrigation due to salinization. As a result of these findings, the researchers responsible for this study suggest that the Jinghuiqu irrigation district should strengthen its groundwater quality management, by limiting use of the elevated sulfate and sodium groundwater for irrigation, or diluting it with low-salinity surface water before use in irrigation. In addition, alternative water-saving irrigation systems should be tested and adapted in the future in the Jinghuiqu irrigation district. By using less water for irrigation purposes, there will be less water leaching towards the groundwater; this will reduce impairment of groundwater quality.

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