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ORIGINAL ARTICLE

# Major ion chemistry of groundwater in the extreme arid region northwest China

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**Abstract** The Ejina Basin, located in arid northwest China, is one of the most arid areas in the world. In recent years, rapid development has created a greater demand for water which is increasingly fulfilled by groundwater abstraction. Detailed knowledge of geochemical evolution of groundwater and water quality can improve the understanding of a hydrochemical system, and promote sustainable development and effective management of groundwater resources. To this end, a hydrochemical survey was conducted in the Ejina Basin in order to identify the major hydrochemical characteristics. The results of chemical analysis indicate that groundwater in the area is brackish. The major ions, TDS, and hydrochemical types of different areas are highly variable and show an obvious zonation from the recharge area to the discharge area. Saturation index (SI), calculated according to the ionic ration plot, indicates that the gypsum-halite dissolution reactions take place under the condition of the rock weathering to some extent, and evaporation is the dominant factor to determine the major ionic composition in the study area.

**Keywords** Hydrochemical · Major ions · TDS · Groundwater · Ejina Basin · Northwest China

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## Introduction

In the arid northwest of China, water resources play a key role in the development of the economy. Careful management is important for ecological and environmental reasons (Gao and Li 1990; Cheng and Qu 1992; Feng et al. 2000). Ejina Basin located in the lower reaches of Heihe River (Fig. 1), is one of the most arid areas in the world. Because of overexploitation of water resources in the middle reaches of Heihe River, the released water volume has decreased acutely from the 1960 s, especially from more than 10 years ago. Heihe River flows only a few days a year in the district, groundwater as only water source has been extensively used to meet the increasing demand for domestic, irrigational and industrial requirements. Due to excessive use of surface water and excessive abstraction of groundwater, local springs have dried up and water levels have been significantly lowered. The quality of groundwater has also been affected by over abstraction (Wang et al. 1999; Tang and Zhang 2001).

In many areas, particularly arid and semi-arid zones, groundwater quality limits the supply of potable fresh water. To utilize and protect valuable water resources effectively and predict the change in groundwater environments, it is necessary to understand the hydrochemical characteristics of the groundwater and its evolution under natural water circulation processes (Lawrence et al. 2000; Edmunds et al. 2002, 2006; Guendouz et al. 2003; Wen et al. 2005; Ma et al. 2005; Ma and Edmunds 2006).

In recent years, the Chinese government and scientists have carried out lots of works on the assessment and utilization of water resource in the Ejina Basin. Many works are focused on evaluating natural water resources, understanding the relationships between water and environment, water and development, and recognizing how to practice

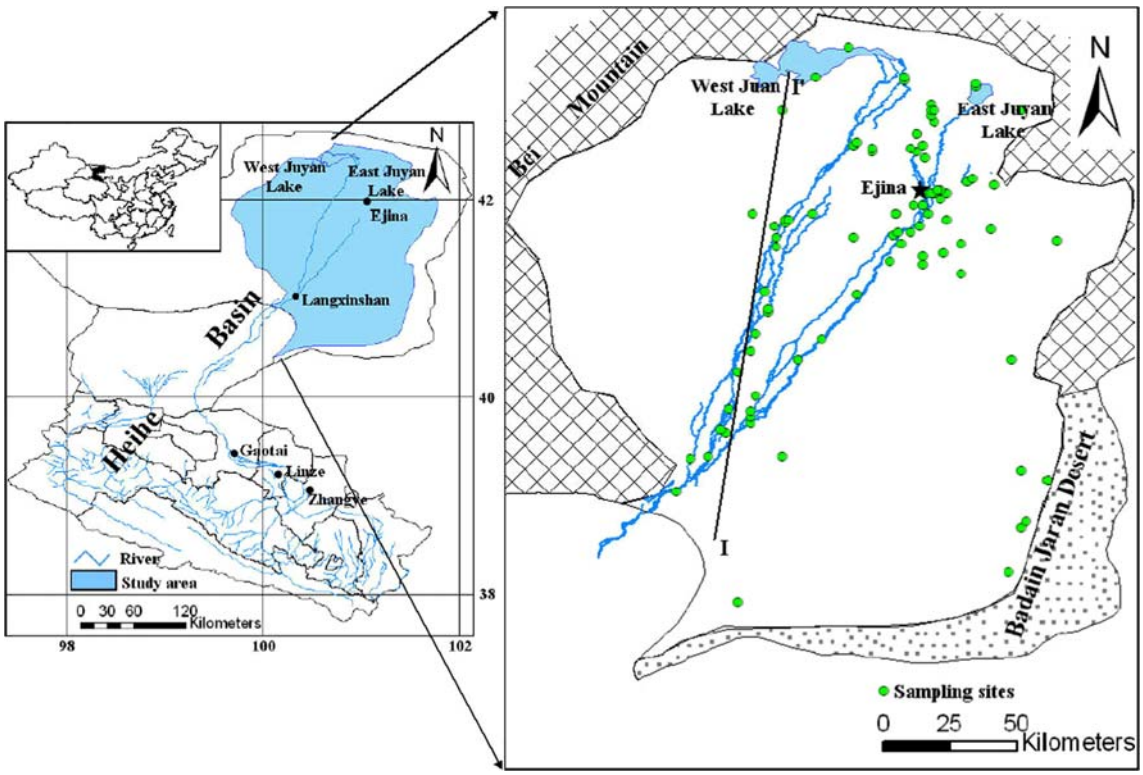


**Fig. 1** Location map of study area and sampling sites

effective water management (Fan 1981, 1990a, b; Gong et al. 1998; Ding et al. 2000; Gao et al. 2004). However, the groundwater quality in the district has received little attention, and efforts to use the geochemistry data available to solve particular problems are even fewer or non-existent. So, the study of the water chemistry of the Heihe River has become a widespread and high priority concern (Feng 1999; Wen et al. 2005). Despite the importance of groundwater in the Ejina Basin, little is known about the natural processes governing the chemical composition of the groundwater or the anthropogenic factors currently affecting it. Increased knowledge on geochemical evolution of groundwater in these arid regions can improve the understanding of hydrochemical systems, and promote sustainable development of water resources and effective management of groundwater resources.

In the present study, a detailed investigation was carried out with the objective of identifying hydrochemical processes and their relation to groundwater quality.

## Materials and methods

### Study site description

Ejina Basin is in the northwest of the Inner Mongolia Autonomous Region, neighboring Youqi of Alashan League to the east, Gansu Province to the south and west, and Mongolia Country to the north. It covers an area of $3 \times 10^4$ km$^2$, extending between latitudes 40°20′–42°30′ N and longitudes 99°30′–102°00′ E. Generally, the ground of the basin slopes from southwest to northeast by degrees, having the feature of low in the middle and high all around. The basin elevations range from 898 to 1,598 m above sea level. Owing to being in the hinterland of Asia Continent, the region has an obvious characteristic of a continental climate that is extremely hot in summer and severely cold in winter, where the mean annual precipitation is 42 mm. The major part of the rainfall (about 60–70%) occurs during July–September. The mean annual potential evaporation is as high as 3,755 mm. Because of sparse precipitation and highly variable, as a consequence, no perennial runoff originates from the area. Hehei River is the only runoff flowing through the study area. Heihe River is one of the greatest inland rivers in China, and Heihe River basin ranges between latitudes 37°45′–42°40′ N to longitudes 96°42′–102°04′ E. The whole basin covers $13 \times 10^4$ km$^2$ area as shown in Fig. 1. Its main stream, with a length of 821 km, originating from the Qilian Mountains of Qinghai Province, flows through the middle basin called the Hexi Corridor of Gansu Province, and reaches the lower reaches known as the Ejina Basin of the Inner Mongolia Autonomous Region. Heihe River is separated into two branches at Langxinshan, the east river and

west river, respectively, flowing north and reaching the east and west of Juyan Lakes.

### Hydrogeological setting

Since Cenozoic, the basin has been filled by unconsolidated Quaternary sediments with a depth of several hundreds of meters and formed a uniform and integrated aquifer system. The basement of basin is Jurassic formation. The southern edge of the basin is the fault of Alashan uplift, and the northern and western edges are naked rock of the mountains, neighboring the hidden fault of Badain Jaran Desert to the east. The Langxinshan–Mujihu uplifts in the north-center of the basin control the distribution of Quaternary sediments and the characteristic of lithofacies. This divides the basin into two aquifer systems. Northwest of the basin is Saihantaolai-Dalaiku settlement area, and the southwest of the basin is Gurinai settlement area. The depositional construction and a variety of lithofacies control the distribution characteristics of aquifer system and the groundwater of the deep confined aquifer system. However, the water table of the shallow aquifer is controlled by topography. From the south to the north of the basin, the lithologic features of the aquifer system gradually vary from gravel to fine sand. The water table gradually becomes shallow. The aquifer system transforms from one layer of phreatic aquifer to several layers of the unconfined–confined aquifer system. One layer of the aquifer is in the south of the basin, and the several layers of the unconfined-confined aquifer system are in the north part of the basin (Fig. 2). The Heihe River in the study area is 240 km long, and seasonal river water is the main source recharging the groundwater. The riverbed is wide and shallow, and the phreatic aquifer consist of coarse sand and gravel with high permeability. About 68% of river water seeps to recharge groundwater in the alluvial fan. The groundwater flows from south to northeastward across the study area. One layer of phreatic aquifer in the southern part of the area is recharged by river water, and groundwater is divided into two flow directions. One is along the Diwandongliang–Langxinshan–Ejina direction flowing from south to north, eventually arriving at the Juyan Lake. The other is along the Diwandongliang–Langxinshan direction flowing toward east to Gurinai, and then flowing toward north to Jinsutuhaizi area (Fig. 3).

Under the natural conditions, evaportranspiration is the main way of the groundwater discharge (Fig. 3). The evaportranspiration of groundwater in phreatic aquifer mainly happened in the northern part of the basin and Gurinai area. The evaportranspiration makes chemical components concentrate in the groundwater, and it causes salt crust in the basin center to occur.

### Major ion chemical analysis

To assess water chemistry values under natural conditions, 91 groundwater samples and 6 surface water samples in the study area were collected during May and October 2006 from long-term groundwater observation wells and drinking wells with depth from 5 to 175 m, as shown in Fig. 1.

Water temperature, electrical conductivity (EC), pH was measured in situ. Chemical components including $SO_4^{2-}$, $HCO_3^-$, $Cl^-$, $NO_3^-$, $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ were measured in the Key Lab in Cold and Arid Regions Environmental and Engineering Research Institute (CAREEI) of Chinese Academy Sciences (CAS). The anions including $SO_4^{2-}$, $Cl^-$, and $NO_3^-$ were analyzed by ion chromatography (Shimadzu), and the anion $HCO_3^-$ was analyzed by titration (pH 4.8 alkalinity). The cations including $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ were analyzed by inductively coupled plasma (ICP-1000 III C, Shimadzu).

## Results and discussion

### Hydrochemical characteristics of surface waters

Heihe River is the only surface water in the study area. The samples were collected at six different sites. The pH value of surface water is 7.5, indicating an alkaline nature. Concentration of TDS varied from 550 to 1,343 mg/L, belonging to the fresh water and slightly saline water. The concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^+ + K^+$, $HCO_3^-$, $Cl^-$, $SO_4^{2-}$, and other ions are shown in Fig. 4. The order of

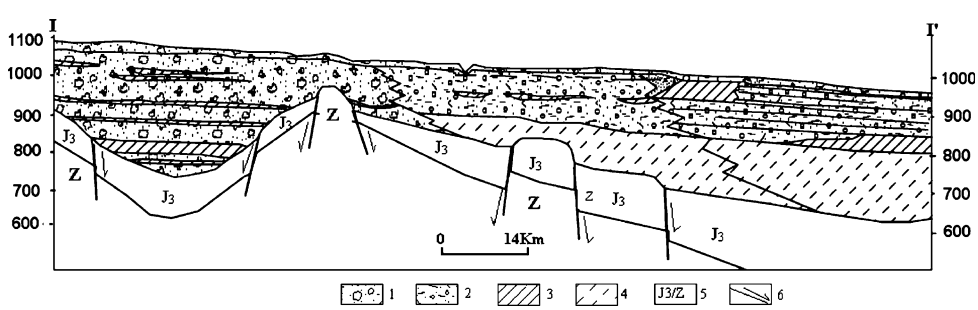


**Fig. 2** Hydrogeological cross section long transect I–I′ as indicated in Fig. 1 (after Wen et al. 2005) *1* gravel, pebble and coarse sand; *2* fine sand; *3* silt; *4* clay; *5* Sinian; *6* Late Jurassic

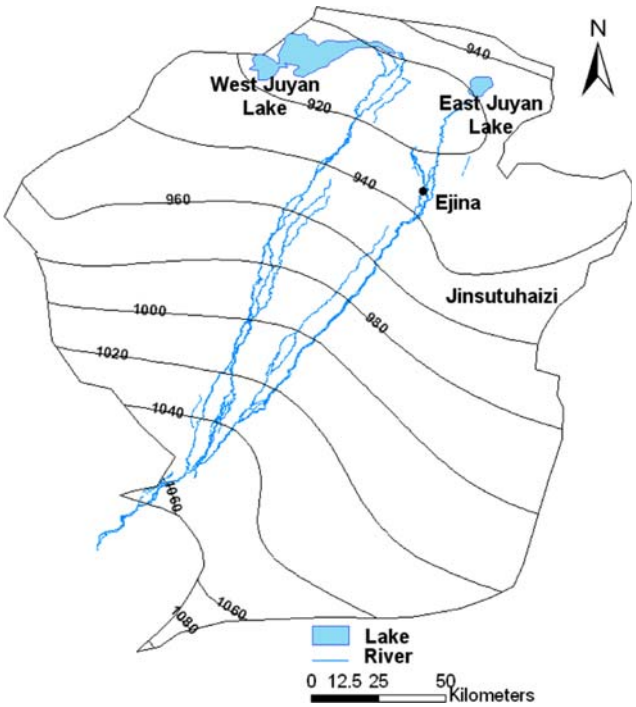


**Fig. 3** Contour of water table in an aquifer system of Ejina basin

cation abundance is $Na^+ + K^+ > Ca^{2+} > Mg^{2+}$, and the order of anion abundance is $SO_4^{2-} > HCO_3^- > Cl^-$. The concentration of ions increases when flow rate of the Heihe River decreases.

## Hydrochemical characteristics of groundwater

### *Major ions chemistry*

The summary statistics for each water quality parameter are given in Table 1. The pH value in groundwater ranges from 7.5 to 8.7 with an average value of 8.1, indicating an alkaline nature. The results of the major ions are plotted in the percentage frequency diagrams of Fig. 5. The relative content of a cation or an anion is defined as the percentage of the milli-equivalent per liter (meq/L) of total cations or total anions. The concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$ range from 0.58 to 19.30%, 0.59 to 27.85%, 2.19 to 48.38%, and 0.07 to 1.64%, with average values of 9.42, 15.70, 24.2, and 0.62%, respectively. The relative concentrations of the cations occurs in the order of $Na^+ + K^+ > Mg^{2+} > Ca^{2+}$. The concentrations of $HCO_3^-$, $Cl^-$ and $SO_4^{2-}$ range from 0.56 to 23.08%, 1.08 to 31.28%, and 11.58 to 35.00%, with average 11.31, 13.91 and 24.78%, respectively. The relative concentrations of the anions occurs in the order of $SO_4^{2-} > Cl^- > HCO_3^-$. No one pair of cations and anions proportions is more than 50% in the shallow groundwater of the study area.

### *Spatial distribution of TDS and major ions*

The TDS concentrations of the groundwater range from 438.39 mg/L to 33,035 mg/L with an average value of 3,509 mg/L (Fig. 6), indicating that the Ejina aquifer contains fresh to very saline waters. TDS components of groundwater in the aquifer vary significantly. TDS and major ions show an obvious special zonation from the recharge areas to the discharge areas as shown in Fig. 6 occurring along the bank of Heihe River. The hydrochemical types of surface water also belong to this type. This type may occur during rapid flow through times, which results in low ionic concentrations during high recharge in shallow zones. This is currently leaving a hydrochemical signature of the surface waters in the groundwater. Concentration of TDS is less than 1,000 mg/L, belonging to fresh water in which $SO_4^{2-}$ and $HCO_3^-$ are the major anions, and $Na^+$ and $Mg^{2+}$ are the major cations. The relative concentrations of the ions occurs in the order of $Na^+ + K^+ > Mg^{2+} > Ca^{2+}$, and $HCO_3^- > SO_4^{2-} >$ Cl or $SO_4^{2-} > HCO_3^- > Cl^-$ from the south to the middle, east and west, in the intermediate zone of groundwater recharge and discharge. The groundwater contains high TDS ranging from 1,000 to 10,000 mg/L, and the groundwater belong to the slightly saline or the moderately saline water in which $SO_4^{2-}$ and $Cl^-$ are the major anions, and the $Na^+$ and $Mg^{2+}$ are the major cations. The relative concentrations of the ions occurs in the order of $Na^+ + K^+ > Mg^{2+} > Ca^{2+}$, and $SO_4^{2-} > Cl^- > HCO_3^-$ or $Cl^- > SO_4^{2-} > HCO_3^-$.

In the west Juyan lake, east Juyan lake and Mujihu area which is the discharge area, the groundwater is with a less active circulation and discharges from strong evaportranspiration. This type of groundwater represents the high TDS with concentration exceeding 10,000 mg/L. The groundwater belongs to the very saline or briny water in which $Cl^-$ is the major anion, and $Na^+$ is the major cation.

### *Groundwater types*

Hydrochemical water types of the study areas are generally distinct, and the dominant anion species of water change systematically from $HCO_3^-$, $SO_4^{2-}$ to $Cl^-$ as groundwater flows from the recharge zone to the discharge zone (Stuyfzand 1999; Toth 1999). According to the Piper diagram (Fig. 7) and proposed diagram (Fig. 8), the geochemical evolution of the groundwater was evaluated. The hydrochemical types in the area can be classed into two major types. First, groundwater in the region is significantly dominated alkaline soil exceed alkali metals and strong acidic anions exceed weak acidic anions. Such water has permanent hardness and does not deposit residual sodium carbonate in irrigation use. The positions of data points in

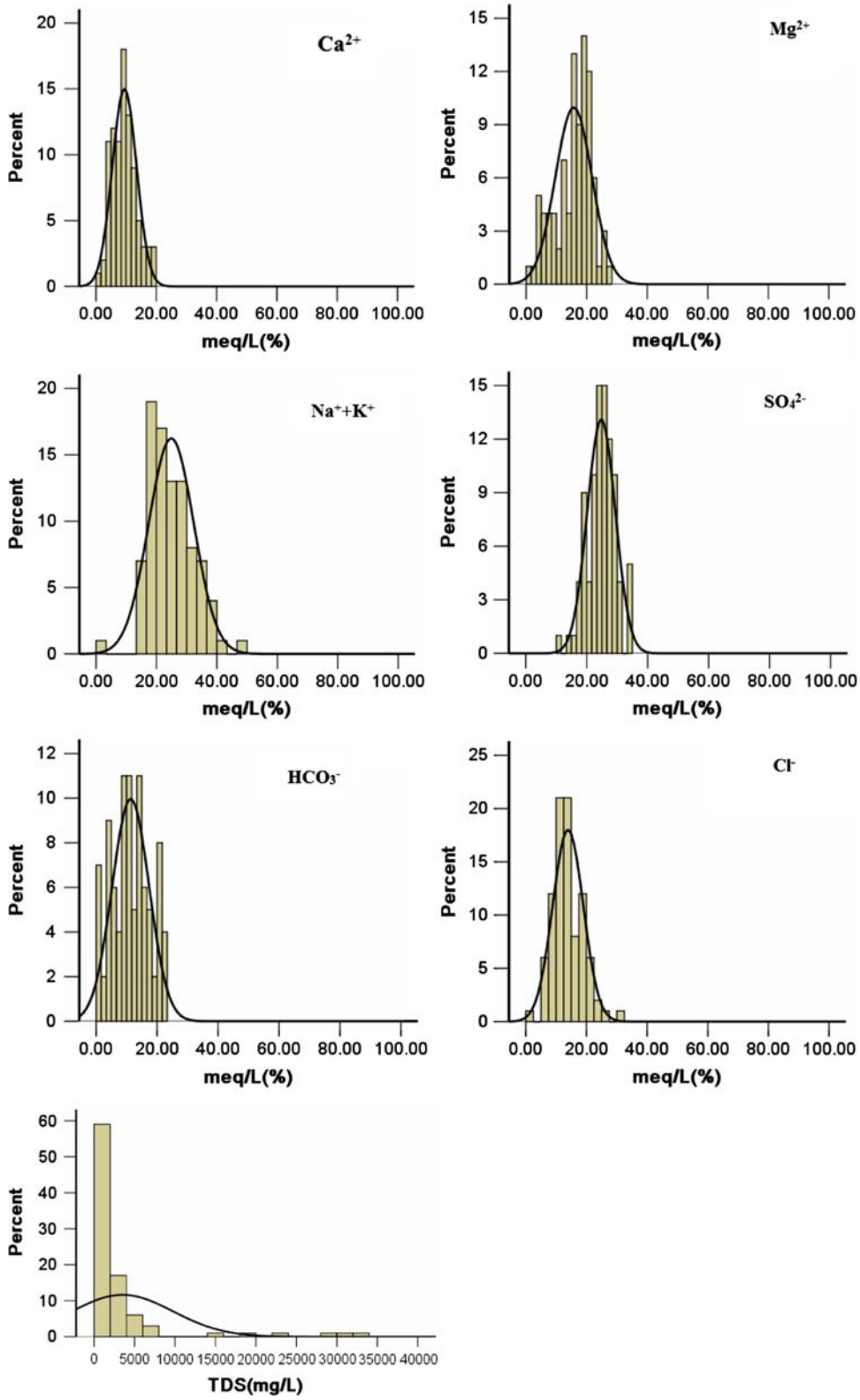


**Fig. 4** Percent frequency distribution of TDS and ion concentrations

the proposed diagram represent $Mg^{2+}$–$Ca^{2+}$–$Cl^{-}$–$SO_4^{2-}$ type, $Mg^{2+}$–$Ca^{2+}$-dominant $Cl^{-}$-type, or $Cl^{-}$-dominant $Mg^{2+}$–$Ca^{2+}$ type waters. These types of water occur along the bank of Heihe River, where is the recharge areas. The hydrochemical types of surface water also belong to this type. This type may occur during rapid flow through times,

**Table 1** Statistical summary of concentrations of chemical constituents, Ejina Basin

| | *N* | Average | Minimum | Maximum | SD |
|---|---|---|---|---|---|
| pH | 91 | 8.06 | 7.53 | 8.74 | 0.20 |
| $HCO_3^-$ (mg/L) | 91 | 370.40 | 114.10 | 1,435.00 | 255.40 |
| $Cl^-$ (mg/L) | 91 | 655.95 | 5.53 | 7,501.00 | 1,374.73 |
| $SO_4^{2-}$ (mg/L) | 91 | 1,467.33 | 122.94 | 15,881.00 | 2,924.13 |
| $Ca^{2+}$ (mg/L) | 91 | 129.79 | 20.40 | 681.00 | 135.81 |
| $Mg^{2+}$ (mg/L) | 91 | 218.74 | 12.50 | 2,494.00 | 433.88 |
| $K^+$ (mg/L) | 91 | 19.05 | 2.00 | 142.00 | 29.41 |
| $Na^+$ (mg/L) | 91 | 585.58 | 13.40 | 5,479.00 | 1,060.41 |
| TDS (mg/L) | 91 | 3,509.57 | 478.39 | 33,035.00 | 6,242.81 |

which results in low ionic concentrations during high recharge in shallow zones. This is currently leaving a hydrochemical signature of the surface waters in the groundwater.

The other type is that alkali metals exceed alkaline soil and strong acidic anions exceed weak acidic anions. Such water generally creates salinity problems both in irrigation and drinking uses. The positions of data points in the proposed diagram represent $Na^+$–$Cl^-$–$SO_4^{2-}$-type, $Na^+$–$SO_4^{2-}$-type, $Na^+$-dominant $Cl^-$-type, or $Cl^-$-dominant $Na^+$-type waters. These types of water occur in the intermediate zone of groundwater recharge and discharge area.

*Hydrochemical evolution*

The major ion relationships in the aquifer are relatively straightforward. Chloride concentrations largely reflect the input conditions at the time of recharge and may be modified subsequently by inputs from forming waters or evaporation (Herczeg and Edmunds 1999). There exists an increase of chloride and sodium ions concentrations along the flow path for the majority of the samples.

The plot of $Na^+$ vs. $Cl^-$ (Fig. 9) shows that the representative points of the aquifer are distributed close to the halite dissolution line. The $Na^+/Cl^-$ weight ratio (Fig. 9) remains relatively constant around $1 \pm 0.5$ which is consistent with stoichiometric dissolution of halite. This suggests a unique origin for these species. However, some samples show sometimes a $Na^+/Cl^-$ ratio that gets further away from unity. Those groundwaters whose ratios are less than 1 generally correspond to waters coming from the bank of Heihe river. They might be affected by the contribution of recent recharge. On the other hand, those waters whose $Na^+/Cl^-$ ratios are larger than 1 match the samples collected in the far away the Heihe River. This fact may be explained by a sodium excess due to ion exchange between water and some minerals notably clayey ones that are present within the aquifer matrix in that area.

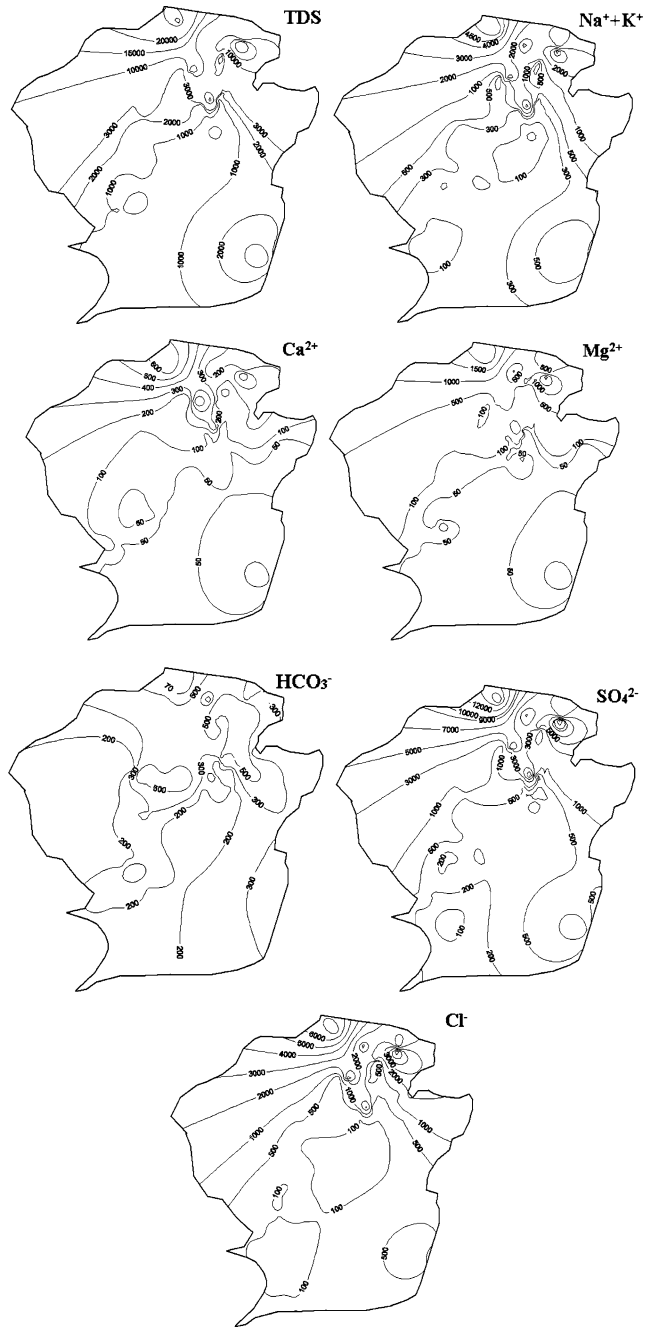


**Fig. 5** Spatial distribution of TDS and major ions in the Ejina Basin

Sulfate concentrations are relatively high in the southern part close to the presumed recharge zone. They exhibit a relative variation along the flowpath from 122 to 15,881 mg/L. These concentrations may be explained by the dissolution of superficial saline gypsum encrustments during recharge and/or irrigation return flow. The high $SO_4^{2-}/Cl^-$ ratio in the study area indicates that the concentrations in these ions are monitored by their respective solubility. It also confirms gypsum dissolution, for which saturation is gradually attained as water flows. On the other

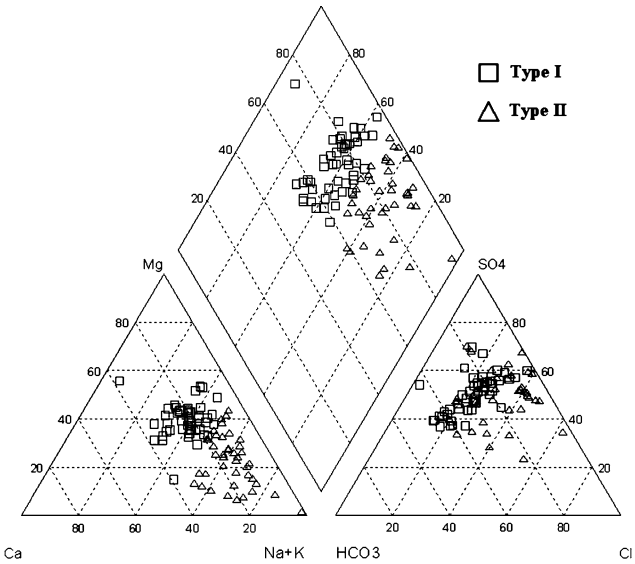


**Fig. 6** Piper diagram of the water samples

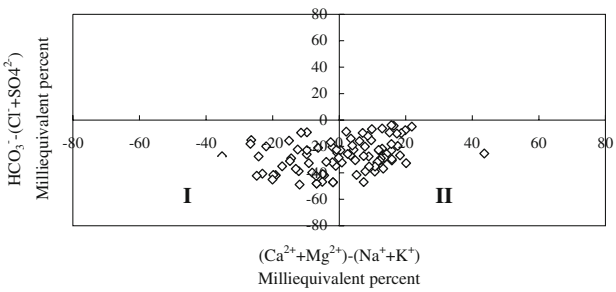


**Fig. 7** Proposed diagram demonstrating geochemical classification and hydrochemical processes of groundwater from Ejina Basin

hand, halite which is more soluble continues to dissolve. Calcium concentrations remain around 24 to 15,881 mg/L in the study area. Nevertheless, a decreasing trend is observed towards the north with $Mg^{2+}/Ca^{2+}$ ratio which becomes larger than 1. The latter may find its origin in a base exchange. Magnesium concentrations show a progressive increase and a good relationship both with sulfates and bicarbonates, which suggests that gypsum and calcite dissolve in parallel.

*Dissolution and deposition*

Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity (Deutsch 1997). If certain minerals such as calcite, dolomite, and magnesite are commonly found in equilibrium with groundwater, it is then reasonable to assume that these minerals are reactive in typical groundwater environments and that they can control solution concentration. By using the saturation index approach, it is possible to predict the

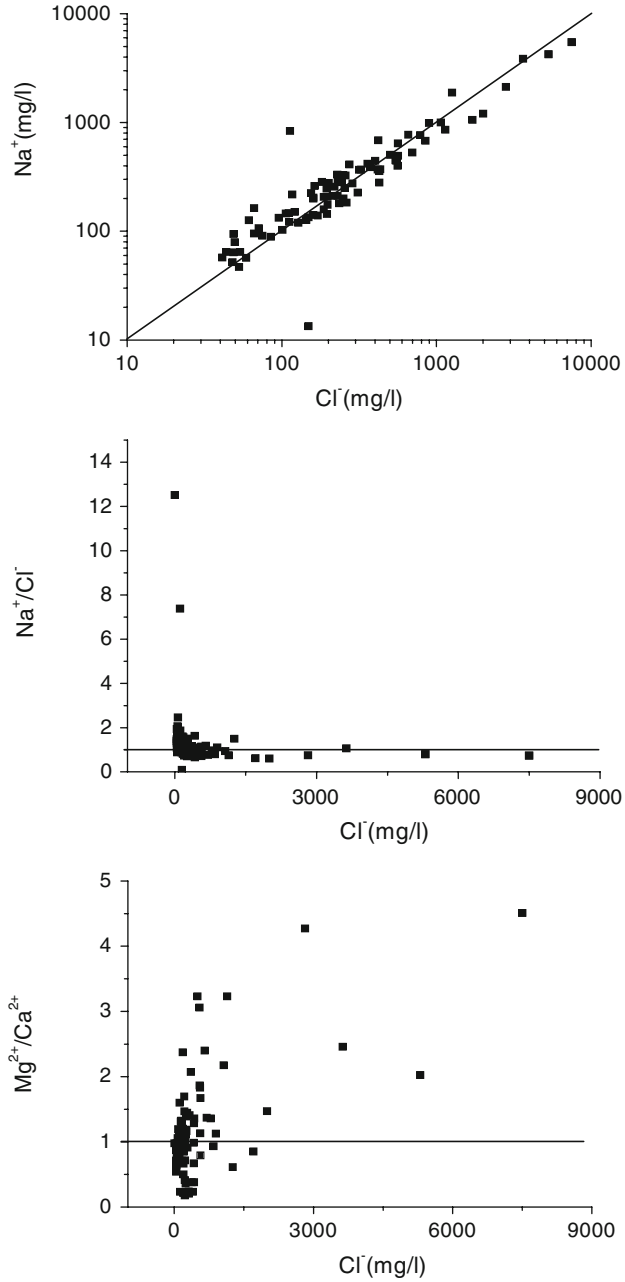


**Fig. 8** Relationship between sodium, Na/Cl, Mg/Ca and $SO_4$/Cl ratios and chloride

reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch 1997). In the present study, to determine the chemical equilibrium between minerals and water, saturation indices (SI) of calcite and dolomite were calculated. If the groundwater is saturated with respect to a mineral, it is prone to deposit (precipitation) some of the solute loads. On the other hand, if it is undersaturated ($SI < 0$) it will take more mineral into the solution (dissolution). Hence, the saturation index of a

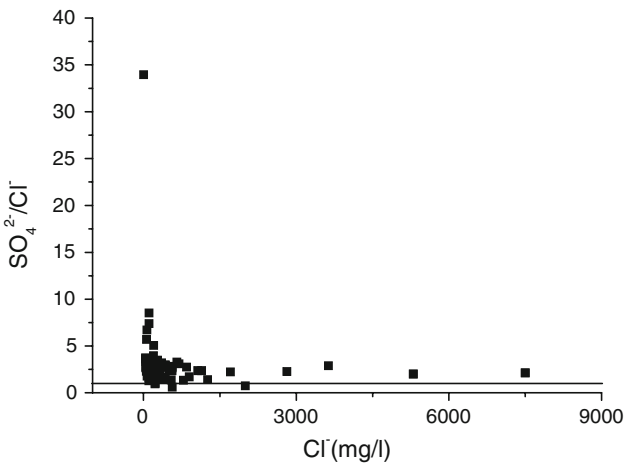


**Fig. 9** Magnesium versus sulfate relationship

mineral is calculated based on the following equation (Lloyd and Heathcode 1985):

$$SI = \log\left(\frac{IAP}{K_S}\right)$$

where IAP is the ion activity product and $K_s$ is the solubility product of the mineral.

The calculated values of SI for calcite, dolomite, magnesite, and gypsum of the groundwater samples range from −0.13 to 1.54, −0.69 to 3.53, −0.86 to 1.96 and −2.00 to 0.17 with average values of 0.74, 1.27, 0.50 and −1.07, respectively. Approximately 80% of SI values for magnesite, 99% of SI values for calcite and 91% of SI dolomite for the groundwater are greater than zero in the water samples. The groundwater is therefore oversaturated with respect to these minerals, and precipitation results. But almost all SI values of gypsum less than zero that show it remain undersaturated. Given the arid climate, this is likely to be a result of evaporation.

## Summary and conclusions

The hydrochemical investigation conducted in the Ejina Basin. According to the percentage frequency diagrams, it shows that no one pair of cations and anions proportions is more than 50% in the groundwater of the study area. TDS and major ions of groundwater are highly variable, and they significantly show a zonation as groundwater flow from recharge area to discharge area. The hydrochemical types in the area can be classed into two major types. One type is that alkaline soil exceeds alkali metals and strong acidic anions exceed weak acidic anions. The other type is that alkali metals exceed alkaline soil and strong acidic anions exceed weak acidic anions.

The $SO_4^{2-}/Cl^-$ ratio remains far greater than 1 over the study area, which suggests that gypsum-halite dissolution reactions take place under the condition of the rock weathering to some extent and evaporation is the dominant factor that determines the major ionic composition in the study area. The SI of calcite, dolomite and magnesite is generally greater than zero in the area, which suggests that these minerals are deposited.

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