

Identifying the origin and geochemical evolution of groundwater using hydrochemistry and stable isotopes in Subei Lake Basin, Ordos energy base, Northwestern China

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Abstract A series of changes in groundwater system caused by groundwater exploitation in energy base have been of great concern to hydrogeologists. The research aims to identify the origin and geochemical evolution of groundwater in Subei lake basin under the influence of human activities. Water samples were collected, major ions and stable isotopes ($\delta^{18}\text{O}$, δD) were analyzed. In terms of hydrogeological conditions and the analytical results of hydrochemical data, groundwater can be classified into three types: the Quaternary groundwater, the shallow Cretaceous groundwater, the deep Cretaceous groundwater. Piper diagram and correlation analysis were used to reveal the hydrochemical characteristics of water resources. The dominant water type of lake water was Na-Cl type, which was in accordance with hydrochemical characteristics of inland salt lake; the predominant hydrochemical types for groundwater were Ca-HCO_3 , Na-HCO_3 , and mixed Ca-Na-Mg-HCO_3 types, the groundwater chemistry is mainly controlled by dissolution/precipitation of anhydrite, gypsum, halite and calcite. The dedolomitization and cation exchange are also important factors. Rock weathering is

confirmed to play a leading role in the mechanisms responsible for the chemical compositions of groundwater. The stable isotopic values of oxygen and hydrogen in groundwater are close to the local meteoric water line, indicating that groundwater is of modern local meteoric origin. Unlike significant difference in isotopic values between shallow groundwater and deep groundwater in Habor lake basin, shallow Cretaceous groundwater and deep Cretaceous groundwater have similar isotopic characteristics in Subei lake basin. Due to evaporation effect and dry climatic conditions, heavy isotopes are more enriched in lake water than groundwater. The low slope of the regression line of $\delta^{18}\text{O}$ and δD in lake water could be ascribed to a combination of mixing and evaporation under conditions of low humidity. By comparison of the regression line for $\delta^{18}\text{O}$ and δD , lake water in Subei lake basin contains more heavily isotopic composition than that in Habor lake basin, indicating that lake water in discharge area has undergone stronger evaporation than lake water in recharge area. The hydrochemical and isotopic information of utmost importance has been provided to decision-makers by the present study so that a sustainable groundwater management strategy could be designed for the Ordos energy base.

Keywords Geochemical evolution; Groundwater; Hydrochemistry; Stable isotopes; Ordos energy base

1. Introduction

The Ordos Basin is located in northwestern China, which covers an area of $28.2 \times 10^4 \text{ km}^2$ in total and comprises the second largest coal reserves in China (Dai et al., 2006). It was authorized as a national energy base in 1998 by the former State Planning Commission (Hou et al., 2006). More than 400 lake basins with diverse sizes are distributed in the Ordos Basin. The Dongsheng-shenfu Coalfield, situated in Inner Mongolia Autonomous Region, is an important component of the Ordos energy base. It is the largest explored coalfield with an enormous potential for future development. The coal reserves explored is 230 billion tons. The coal is exploited from Jurassic strata and subsurface mining is common. Local residents there mostly depend on groundwater on account of the serious shortage of surface water. Water resources support the exploitation of coal and development of related industries. In China, all

new construction projects must carry out groundwater environment evaluation in consistent with the technical guidelines of the PRC Ministry of Environmental Protection (2011) since 2011. It is of most significance in mining areas, because water resource is an essential component of the mining process (Agartan and Yazicigil, 2012). Over the past several decades, the quantity and quality of groundwater resources have been affected by the rapid development of coal mining. Haolebaoji well field of Subei lake basin is a typical, large well field and acts as an important source of water-supply in this coalfield. However, large-scale and intensive groundwater exploitation could remarkably influence hydrodynamic field and hydrochemical field of groundwater system in the study area. In recent years, with the fast development of Ordos energy base, more and more well fields have been built in some lake basins (including Haolebaoji well field newly built in Subei lake basin) in order to meet the increasing demand of water resources, but due to lack of adequate hydrogeological knowledge about these specific lake basins and reasonable groundwater management strategy, water resources in these specific lake basins are currently subject to increasing pressure from altered hydrology associated with water abstraction for regional development and groundwater over-exploitation has taken place. If it continues, it may cause a series of negative impacts on the groundwater-dependent ecosystem around these lakes. So studies about the lake basins are urgently needed so as to obtain a comprehensive knowledge of the hydrochemical and isotopic characteristics, and geochemical evolution of groundwater under the background of intensive groundwater exploitation.

The research of groundwater and hydrogeology in the Ordos Basin has been conducted by a lot of Chinese scholars and institutes because they play a vital role in natural resources exploitation and national economic development. Above all, China Geological Survey Bureau has conducted some regional-scale research on groundwater resources of Ordos Basin since 1980s (Zhang et al., 1986; Hou et al., 2008). These research clarified geology, hydrogeology and a comprehensive knowledge of quantity and quality of groundwater in this region, which laid a solid foundation for the present study. However, regional-scale groundwater investigations

may not provide much accurate information on the groundwater flow characteristics in small basin (Toth, 1963). Hence, it is also significant to implement local groundwater resources investigations. As Winter (1999) concluded that lakes in different part of groundwater flow systems have different flow characteristics. Data on hydrochemistry and stable isotopes of water were used to study the origin and geochemical evolution of groundwater in the Habor lake basin (Yin et al., 2009), which is located in recharge zone. But other lakes in the runoff and discharge area still have not been studied so far. Due to the particularity of discharge area, a variety of hydrochemical effects such as evaporation, decarbonation, strong mixing action, etc., take place and result in extremely complicated hydrochemical and isotopic characteristics of discharge area. In addition, intensive groundwater withdrawal has dramatically changed the local hydrologic cycle in these specific lake basins, groundwater flow field and hydrochemistry have been changed significantly, a series of ecological environment problems have taken place. Therefore, given that the potential problems brought by human activity, it is essential to conduct hydrochemical and isotopic study of Subei lake basin located in discharge area.

Isotopic and geochemical indicators often serve as effective methods for solving multiple problems in hydrology and hydrogeology, especially in the semi-arid and arid regions (Clark and Fritz, 1997; Cook and Herczeg, 1999). These techniques have been widely used to obtain groundwater information such as its source, recharge and the interaction between groundwater and surface water (De Vries and Simmers, 2002; Yuko et al., 2002; Yang et al., 2012a). The technique of stable isotopes as excellent tracers, has been widely used by many scholars in the study of hydrological cycle (Chen et al., 2011; Cervi et al., 2012; Garvelmann et al., 2012; Yang et al., 2012a; Hamed and Dhahri, 2013; Kamdee et al., 2013). The origin and behavior of major ions in groundwater can enhance understanding of geochemical evolution of groundwater, measurement of the relative concentration of major ions in groundwater from different aquifers can provide information on the geochemical reactions within the aquifer and the possible evolutionary pathways of groundwater (Cook and Herczeg, 1999).

The aim of the research is to recognize the origin and geochemical evolution of groundwater in Subei lake basin under the influence of human activities. The main objectives are to (1) ascertain the origin of groundwater, (2) determine the geochemical factors and mechanisms controlling the chemical composition of groundwater. In the context of a large number of well fields built in some lake basins in order to meet the increasing demand of water resources, the results of the present study will be valuable in obtaining a deeper insight into hydrogeochemical changes caused by human activity, and providing significant information such as water quality situation and geochemical evolution of groundwater to decision makers so that they can make sustainable groundwater management strategies for other similar small lake basins and even the Ordos energy base.

2. Study Area

2.1 Physiography

The study area is situated in the northern part of the Ordos Basin, which is located at the junction of Wushen County, Hangjin County and Yijinhuluo County in Ordos City and is mainly administratively governed by Wushen County of Ordos City. It almost covers an area of 400 km², ranging within latitudes 39°13'30"-39°25'40"N and longitudes 108°51'24"-109°08'40"E. Its length is 23km from east to west and its width is 22km from north to south (Fig.1).

The continental semi-arid to arid climate controls the whole study area, which is characterized by long, cold winters and short, hot summers (Li et al., 2010;Li et al., 2011). According to the data of Wushenzhao meteorological station, the average monthly temperature ranges from -11.5°C in January to 21.9°C in July. The mean annual precipitation in study area is 324.3mm yr⁻¹ from 1985-2008, the total annual precipitation varied greatly from year to year with a minimum 150.2mm in 2000 and a maximum 432.3mm in 1985. A majority of the precipitation falls in the form of rain during the 3-month period from June to August, when precipitation accounts for more than 63.6% of annual precipitation (Fig.2). The mean annual evaporation is 2349.1mm yr⁻¹ (from 1985 to 2008) at Wushenzhao station (Fig.2), which far exceeds

rainfall for the area. The average value of monthly evaporation is lowest in January (42.4mm month⁻¹) and highest from May to July with a maximum evaporation in May (377.4mm month⁻¹).

As a small-scale lake basin, the main geomorphic types of Subei lake basin are wavy plateau, lake beach and sand dune from an overall perspective (Fig.1). The terrain of Subei lake's west, east, north side is relatively higher with altitudes between 1370-1415m, the terrain of its south side is slightly lower with elevations between 1290-1300m. The topography of the center area is flat and low-lying, where Subei lake exists. There are no perennial or ephemeral rivers within the study area; the only surface water body is Subei lake and Kuisheng lake, and they are situated in the same watershed in consideration of actual hydrogeological conditions and groundwater flow field. In response to precipitation, diffuse overland flow and groundwater recharge the Subei lake and Kuisheng lake (Hou et al., 2006 ;Wang et al., 2010). Subei lake is located in the low-lying center of the study area (Fig.1), which is an inland lake characterized by high alkalinity; Kuisheng lake is also a perennial water body and it is located in northeastern corner of the study area, only covering 2km² (Fig.1).

2.2 Geologic and hydrogeologic setting

Subei lake basin is a relatively closed hydrogeological unit given that a small quantity of lateral outflow occurs in a small part of southern boundary (Wang et al., 2010). The Quaternary sediments and Cretaceous formation can be observed in the study area. The Quaternary sediments are mainly distributed around the Subei lake with relatively smaller thickness, generally the thickness of Quaternary sediments is below 20m. The Quaternary layer is chiefly composed of the interlaced layers of sand and mud. The Cretaceous formations mainly consist of sedimentary sandstones and generally outcrop in the regions with relatively higher elevation. The maximum thickness of Cretaceous rocks could be nearly 1000m in the Ordos Plateau (Yin et al., 2009), so the Cretaceous formation composed of mainly sandstone is the major water-supply aquifer of the investigated area. Calcite, dolomite, anhydrite, aragonite, gypsum, halite, and feldspar are major minerals in the Quaternary and Cretaceous

strata (Hou et al., 2006).

Groundwater resources are very abundant in the investigated area and phreatic aquifer and confined aquifer could be observed in this region. According to Wang et al. (2010) and the data from Inner Mongolia Second Hydrogeology Engineering Geological Prospecting Institute, the phreatic aquifer is composed of Quaternary and Cretaceous sandstones, with its thickness ranging from 10.52m to 63.54m. In terms of borehole data, the similar groundwater levels in the Quaternary and Cretaceous phreatic aquifers indicate a very close hydraulic connection between the Quaternary layer and Cretaceous phreatic aquifer, which could be viewed as an integrated unconfined aquifer in the area. The depth to water table in unconfined aquifer is influenced by the terrain change, of which, the minimum value is below 1m in low-lying region and the maximum value could be up to 13.24m. The hydraulic conductivity of the aquifer changes between 0.16m/d and 17.86m/d. The specific yield of unconfined aquifer varies from 0.058 to 0.155. The recharge source of groundwater in unconfined aquifer is mainly the infiltration recharge of precipitation; it can be also recharged by lateral inflow from groundwater outside the study area. Besides the above recharge terms, leakage recharge from the underlying confined aquifer and infiltration recharge of irrigation water can also provide a small percentage of groundwater recharge. Evaporation is the main discharge way of the unconfined groundwater. In addition, lateral outflow, artificial exploitation and leakage discharge are also included in the main discharge patterns. Unconfined groundwater levels were contoured to illustrate the general flow field in the area (Fig.3). Groundwater levels were monitored during September 2003. As is shown in Fig.3, lateral outflow occurs in a small part of southern boundary by analyzing the contours and flow direction of groundwater. The groundwater flows predominantly from surrounding uplands to low lands, which is under the control of topography. On the whole, groundwater in phreatic aquifer flows toward Subei lake and recharges lake water (Fig.3).

The unconfined and confined aquifers are separated by an uncontinuous aquitard. Generally speaking, permeable layers and aquitards intervein in the vertical profile of

the aquifer system. Nevertheless, aquitards may pinch out in many places, so the aquifer system acts as a single hydrogeologic unit. In the present study, the covering aquitard is composed of the mudstone layer, which is mainly distributed in the second sand layer, and discontinued mudstone lens also could be observed in Cretaceous strata (Fig.4). The phreatic aquifer is underlain by confined aquifer composed of Cretaceous rocks. Due to huge thickness and high permeability of confined aquifer, it is regarded as the most promising water-supply aquifer for domestic and industrial uses. The hydraulic conductivity of confined aquifer changes between 0.14m/d and 27.04m/d. The hydraulic gradient varies from 0.0010 to 0.0045 and the storage coefficient changes between 2.17×10^{-5} and 1.98×10^{-3} . The confined aquifer primarily receives leakage recharge from the unconfined groundwater. The flow direction of confined groundwater is similar to that of unconfined groundwater (Fig.3). Artificial exploitation is the major drainage way of confined groundwater.

In the present study, the depth of sampling wells is used to classify groundwater as Quaternary groundwater, shallow Cretaceous groundwater and deep Cretaceous groundwater in combination with hydrogeological map of the study area. As a research on an adjacent, specific shallow groundwater system of Ordos Basin shows that the circulation depth is 120m (Yin et al., 2009). It is difficult to determine the circulation depth of shallow groundwater in fact because the circulation depth of local flow systems is changeable dependent on the topography and the permeability of local systems (Yin et al., 2009). In this study, Quaternary groundwater was defined on the basis of the distribution of Quaternary sediments thickness and depth of sampling wells. According to Hou et al. (2006), the maximum circulation depth of local groundwater flow system in the study area is also 120m by using a plenty of hydrochemical and isotopic data, 120m is chosen as the maximum circulation depth of local groundwater system and is used to divide the Cretaceous groundwater samples into two groups, samples taken in wells shallower than 120m were classified as shallow Cretaceous groundwater, while samples taken in wells deeper than 120m were deep Cretaceous groundwater.

3. Methods

3.1 Water sampling

Two important sampling actions were conducted in the study area during August and December 2013, respectively. A total of ninety-five groundwater samples and seven lake water samples were collected. The first sampling action was during rainy season, the other was during dry season. The sampling locations are shown in Fig.5. The water samples were taken from wells for domestic and agricultural purposes ranging in depth from 2m to 300m. The length of screen pipes in all sampling wells ranges from 1m to 10m and every sampling well has only one screen pipe rather than multiple screens. The distance between the bottom of screen pipe and the total well depth ranges from 0 to 3m in the study area, the bottom depth of screen pipe was assigned to the water samples. The samples from the wells were mostly taken using pumps installed in these wells and after removing several well volumes prior to sampling. The 100ml and 50ml polyethylene bottles were pre-rinsed with water sample three times before the final water sample was collected. Lake water samples were collected at Subei lake, Kuisheng lake and Shahaizi. Cellulose membrane filters (0.45 μ m) were used to filter samples for cations and anions analysis. All samples were sealed with adhesive tape so as to prevent evaporation. The global positioning system (GPS) was applied to locate the sampling locations.

3.2 Analytical techniques

Electrical conductivity (EC), pH value and water temperature of each sample were measured in situ using an EC/pH meter (WM-22EP, Toadkk, Japan), which was previously calibrated. Dissolved oxygen concentration and oxidation-reduction potential were also determined using a HACH HQ30d Single-Input Multi-Parameter Digital Meter. In situ hydrochemical parameters were monitored until these values reached a steady state.

The hydrochemical parameters were analyzed at the Center for Physical and Chemical Analysis of Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (IGSNRR, CAS). Major ion compositions

were measured for each sample, K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- included. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima 5300DV, USA) was applied to analyze major cations. Major anions were measured on ion chromatography (ICS-2100, Dionex, USA). HCO_3^- concentration in all groundwater samples was determined by the diluted vitriol-methylic titration method using 0.0048M H_2SO_4 on the day of sampling, methyl orange endpoint titration was adopted with the final pH being 4.2-4.4. Due to extremely high alkalinity of lake water samples, HCO_3^- concentration in all lake water samples was analyzed by titration using 0.1667M H_2SO_4 . CO_3^{2-} concentration was also analyzed by titration method, phenolphthalein was used as an indicator of endpoint titration.

Hydrogen (δD) and oxygen ($\delta^{18}O$) composition in the water samples were analyzed using Liquid Water Isotope Analyzer (LGR, USA) at the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (IGSNRR, CAS). Results were expressed in the standard δ -notation as per mil (‰) difference from Vienna standard mean ocean water (VSMOW, 0‰) with analytical precisions of $\pm 1\text{‰}$ (δD) and $\pm 0.1\text{‰}$ ($\delta^{18}O$).

4. Results

4.1 Hydrochemical characteristics

In situ water-quality parameters such as pH, electrical conductivity (EC), temperature, dissolved oxygen concentration (DO), oxidation-reduction potential (ORP) and total dissolved solids (TDS) as well as analytical data of the major ions composition in groundwater, lake water samples are shown in Table 1 and Supplementary Table S1. Based on the chemical data, hydrochemical characteristics of groundwater and lake water are discussed.

The chemical composition for lake water showed that Na^+ averagely accounted for 93% of total cations and Cl^- averagely accounted for 58% of total anions. So Na^+ and Cl^- were the dominant elements (Fig.6), which was in accordance with hydrochemical characteristics of inland salt lake. This was also observed in lake water

of Habor lake basin located in recharge area (Yin et al., 2009). The pH of lake water varied from 8.86 to 10.25 with an average of 9.74 in August and changed from 8.49 to 10.47 with an average of 9.23 in December, it can be seen that the pH was relatively stable and was always more than 8.4 without obvious seasonal variation, which indicated the dissolved carbonates were in the HCO_3^- and CO_3^{2-} forms simultaneously. The temperatures of lake water ranged from 1.1°C to 24.3°C with a large seasonal variation, which reflected that surface water body was mainly influenced by hydrometeorological factors. Dissolved oxygen concentration of lake water showed an upward tendency from August (mean value: 11.50mg/L) to December (mean value: 14.27mg/L), because the relationship between water temperature and DO is inverse when oxygen content in the air stays relatively stable. With the decreasing water temperature, dissolved oxygen value rises. The average value of ORP ranged from 15.1mV in August to 26.8mV in December, which was in accordance with the upward tendency of DO. It showed that lake water had stronger oxidation in December than that in August and there is a close relationship between DO and ORP. The average values of major ions concentrations showed a downward trend except Ca^{2+} , Mg^{2+} from August to December. Specifically, the average values of Ca^{2+} and Mg^{2+} increased from 6.50 to 15.30mg/L, 25.15 to 102.20mg/L, respectively, other ions concentrations reduced in different degree. The same variation trend of major ions from August to December could be found in Habor lake basin (Yin et al., 2009) as well. Before August, the strong evaporation capacity of lake water exceeded the finite recharge amount, which caused lake water to be enriched. After August, lake water was recharged and diluted by groundwater and a plenty of fresh overland flow in response to precipitation. The EC values varied between 1017 and 229 000 $\mu\text{S}/\text{cm}$. This relatively large range of variation was closely related to the oscillation of the TDS values, which ranged from 0.56 to 302.5g/L. The results showed that lake water chemistry was controlled by strong evaporation and recharge from overland flow and groundwater.

The hydrochemical data of groundwater were plotted on a Piper triangular diagram (Piper, 1953), which is perhaps the most commonly used method for

identifying hydrochemical patterns in major ion composition (Fig.6). With respect to cations, most of samples are scattered in zones A, B and D of the lower left triangle, indicating that some are calcium-type, some are sodium-type water, but most of all are mixed-type, as regards anions, most groundwater samples are plotted in zone E of the lower right triangle (Fig.6), showing that bicarbonate-type water is predominant. The predominant hydrochemical types are Ca-HCO_3 , Na-HCO_3 and mixed Ca-Na-Mg-HCO_3 types. Figure 6 also indicates that there are three groups of groundwater in Subei lake basin: the Quaternary groundwater, shallow Cretaceous groundwater, and deep Cretaceous groundwater. The shallow Cretaceous groundwater refers to groundwater in local groundwater system, and the deep Cretaceous groundwater refers to groundwater in intermediate groundwater system of Ordos basin. The hydrochemical characteristics of the three groups of groundwater indicate that they have undergone different degrees of mineralization processes.

With respect to the Quaternary groundwater, the pH varied from 7.64 to 9.04 with an average of 8.09 in August and changed from 7.49 to 9.26 with an average of 8.08 in December, indicating an alkaline nature. The TDS varied from 396 to 1202mg/L, 314 to 1108mg/L with averages 677mg/L and 625mg/L, respectively in August and December. The major cations were Na^+ , Ca^{2+} and Mg^{2+} , while the major anions were HCO_3^- and SO_4^{2-} .

As for the shallow Cretaceous groundwater (<120m), the pH varied from 7.37 to 8.3 with an average of 7.77 in August and oscillated from 7.49 to 9.37 with an average of 8.14 in December. The TDS varied from 249 to 1383mg/L, 217 to 1239mg/L with averages 506 mg/L and 400mg/L, respectively in August and December.

For the deep Cretaceous groundwater (>120m), the pH varied from 7.75 to 8.09 with an average of 7.85 in August and fluctuated from 7.99 to 8.82 with an average of 8.23 in December. The TDS varied from 266 to 727mg/L, 215 to 464mg/L with averages 377 mg/L and 296mg/L, respectively in August and December.

4.2 Stable isotopic composition in groundwater and surface water

In the present study, the results of the stable isotope analysis for groundwater and lake water were plotted in Fig.7. In previous study, the local meteoric water line

(LMWL) in the northern Ordos Basin had been developed by Yin et al. (2010). The LMWL is $\delta D = 6.45\delta^{18}O - 6.51$ ($r^2 = 0.87$), which is similar to that developed by Hou et al. (2007) ($\delta D = 6.35\delta^{18}O - 4.69$). In addition, it is very clear in the plot that the LMWL is located below the global meteoric water line (GMWL) defined by Craig (1961) $\delta D = 8\delta^{18}O + 10$, which suggests the occurrence of secondary evaporation during rainfall. The LMWL is controlled by local hydrometeorological factors, including the origin of the vapor mass, re-evaporation during rainfall and the seasonality of precipitation (Clark and Fritz, 1997).

The linear regression curve equation of $\delta^{18}O$ and δD in groundwater can be defined as $\delta D = 6.3\delta^{18}O - 13.0$ ($r^2 = 0.62$). Groundwater follows the LMWL in the study area, indicating that it is of modern local meteoric origin rather than the recharge from precipitation in paleo-climate conditions. In August, the stable isotope values in the Quaternary groundwater were found to range from -9.2 to -8.0‰ in ^{18}O with an average of -8.8‰ and from -74 to -62‰ in 2H with an average of -71‰; the shallow Cretaceous groundwater had $\delta^{18}O$ ranging from -9.3 to -7.5‰ and δD varying from -75 to -57‰. The average values of $\delta^{18}O$ and δD of the shallow Cretaceous groundwater were -8.3 and -66‰, respectively. $\delta^{18}O$ and δD of the deep Cretaceous groundwater ranged from -9.3 to -7.8‰ and from -74 to -61‰, respectively. The average values of $\delta^{18}O$ and δD were -8.4 and -67‰, respectively. In December, the stable isotope values in the Quaternary groundwater ranged from -8.9 to -7.2‰ in ^{18}O with an average of -8.2‰ and from -74 to -57‰ in 2H with an average of -65‰; $\delta^{18}O$ and δD of the shallow Cretaceous groundwater ranged from -9.7 to -6.5‰ and from -73 to -58‰, respectively. The average values of $\delta^{18}O$ and δD were -8.2 and -64‰, respectively. The deep Cretaceous groundwater had $\delta^{18}O$ varying from -10.0 to -7.5‰ and δD varying from -75 to -60‰. The average values of $\delta^{18}O$ and δD of the deep Cretaceous groundwater were -8.5 and -66‰, respectively.

The regression curve equation of $\delta^{18}O$ and δD in lake water could be defined as $\delta D = 1.47\delta^{18}O - 29.09$ ($r^2 = 0.95$), where $\delta^{18}O$ ranged from -5.8 to 29.4‰ and δD ranged from -46 to 15‰ with averages 14.3 and -10‰ in August; while in December, $\delta^{18}O$ and δD of lake water ranged from -2.6 to 16.2‰ and from -28 to -9‰, respectively.

The average values of $\delta^{18}\text{O}$ and δD were 4.4 and -21‰, respectively in December. The low slope of the regression line of $\delta^{18}\text{O}$ and δD in lake water could be ascribed to a combination of mixing and evaporation under conditions of low humidity.

4.3 Linkage among geochemical parameters of groundwater

Correlations among groundwater-quality parameters are shown in Table 2 and Fig.8. All of the major cations and anions are significantly correlated with TDS (Table 2), which shows that these ions have been dissolved into groundwater continuously, and then resulted in the rise of TDS.

As is shown in Table 2, the concentration of Mg^{2+} is correlated with HCO_3^- and SO_4^{2-} , with correlation coefficients of 0.582 and 0.819, respectively. The concentration of Ca^{2+} is well correlated with SO_4^{2-} with a correlation coefficient of 0.665. Cl^- has a good correlation with Na^+ with a large correlation coefficient of 0.824.

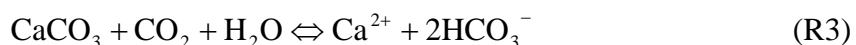
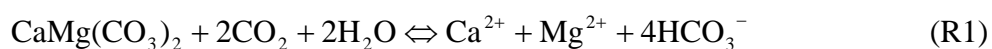
Linear regression analytical results of some pairs of ions are displayed in Fig.8. There is a good correlation between Cl^- and Na^+ in Quaternary groundwater and shallow Cretaceous groundwater; Ca^{2+} and SO_4^{2-} have a good positive correlation in Quaternary groundwater and shallow Cretaceous groundwater. Mg^{2+} is well correlated with HCO_3^- in shallow Cretaceous groundwater.

5. Discussion

Generally speaking, water-rock interactions are the most important factors of influencing the observed geochemical composition of groundwater (Appelo and Willemsen, 1987), the geochemical and isotopic results of this work are no exceptions. In terms of dissolved minerals and the correlation of geochemical parameters, the dominant geochemical processes and formation mechanisms could be found (Su et al., 2009). The weathering and dissolution of minerals in the host rocks and ion exchange are generally the main source of ions in groundwater on a basis of available research. The stable isotopes signatures in lake water can reveal the predominant mechanism controlling the chemical composition of lake water.

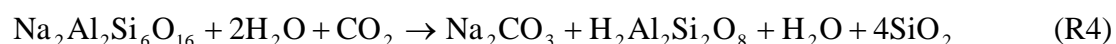
5.1 Geochemical processes of groundwater

As displayed in the correlation analysis of geochemical parameters, a good correlation between Mg^{2+} and HCO_3^- indicates that the weathering of dolomite releases ions to the groundwater, as expressed in reaction (R1). The fact that Mg^{2+} is well correlated with HCO_3^- could be found in Habor lake basin of Ordos plateau (Yin et al., 2009). Ca^{2+} has a good correlation with SO_4^{2-} , implying that the dissolution of gypsum and anhydrite may be the key processes controlling the chemical composition of groundwater in discharge area, which can be explained by reaction (R2). Just as the achievements obtained by Hou et al. (2006), gypsum and anhydrite are present in these strata, so it is reasonable to consider that gypsum and anhydrite are the source of the SO_4^{2-} . However, in Yin's study, there is not a good correlation between Ca^{2+} and SO_4^{2-} in Habor lake basin (Yin et al., 2009). It can be explained by geochemical evolution of groundwater along flow path from the recharge area to the discharge area. There is not a good correlation between Na^+ and SO_4^{2-} , suggesting that weathering of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) may not be the major sources of such ions in groundwater. On the contrary, a good correlation between Na^+ and SO_4^{2-} can be found in Habor lake basin (Yin et al., 2009). It indicates that Glauber's salt may be more abundant in recharge area (Habor lake basin) than in discharge area (Subei lake basin). Although there is no obvious correlation between Ca^{2+} and HCO_3^- , it is reasonable to regard the dissolution of carbonate minerals as a source of Ca^{2+} and HCO_3^- due to widespread occurrence of carbonate rocks in the study area, as conveyed in reaction (R3). The concentration of Mg^{2+} is well correlated with SO_4^{2-} , suggesting the potential, possible dissolution of gypsum, followed by cation exchange. The pH is negatively correlated with Ca^{2+} , it is likely that the dissolution of carbonate minerals is constrained due to the reduction of hydrogen ion concentration in water at higher pH. It could be judged from the above analysis that during groundwater flow, the following reactions are very likely to take place in the study area:



In order to explore the mechanism of salinity in semi-arid regions, the plot of Na^+ versus Cl^- is widely used (Magaritz et al., 1981; Dixon and Chiswell, 1992; Sami, 1992). The concentration of Cl^- is well correlated with Na^+ , suggesting that the dissolution of halite may be the major source of Na^+ and Cl^- . Theoretically, the dissolution of halite will release equal amounts of Na^+ and Cl^- into the solution. Nevertheless, the results deviate from the anticipated 1:1 relation. Almost all samples have more Na^+ than Cl^- . The molar Na/Cl ratios vary from 0.68 to 16.00 with an average value of 3.48. Greater Na/Cl ratios may be ascribed to the feldspar weathering and the dissolution of other Na-containing minerals. The relatively high Na^+ concentration in the groundwater could also be illustrated by cation exchange between Ca^{2+} or Mg^{2+} and Na^+ , as is discussed later.

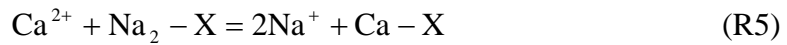
The partial pressure of carbon dioxide (pCO_2) values were calculated by the geochemical computer code PHREEQC (Parkhurst and Appelo, 2004). The pCO_2 values of groundwater range from $10^{-0.82}$ to $10^{-4.1}$ atm. The vast majority of groundwater samples (about 96%) have higher pCO_2 values than the atmospheric pCO_2 that is equal to $10^{-3.5}$ atm (Van der Weijden and Pacheco, 2003), indicating that groundwater has received CO_2 from root respiration and the decomposition of soil organic matter. Figure 9 indicates that the pCO_2 values are negatively correlated with pH values, the partial pressure values of CO_2 decrease as pH values increase (Rightmire, 1978; Adams et al., 2001). It is likely to have a connection with relatively longer aquifer residence time, more physical, chemical reactions with aquifer minerals and biological reactions of microorganism that produce CO_2 will take place. According to Hou et al. (2008), feldspars can be observed in the Cretaceous formations and the following reaction possibly occurs.



This reaction will consume CO_2 and give rise to the increase of the concentration of Na^+ and HCO_3^- . As a result, partial pressure of CO_2 will decrease and the pH will increase. In terms of a statistical analysis, the average pH values of the Quaternary groundwater and the shallow Cretaceous groundwater are 8.08 and 7.99 respectively,

lower than that of the deep Cretaceous groundwater (8.11). However, the average pCO₂ values of the Quaternary groundwater and the shallow Cretaceous groundwater are 10^{-2.67} and 10^{-2.58} atm respectively, being higher than that of the deep Cretaceous groundwater (about 10^{-2.79} atm). The negative correlation characteristic between pCO₂ and pH shows that the dissolution of feldspar does take place along groundwater flow path. The phenomenon also occurs in Habor lake basin according to Yin et al. (2009).

Cation exchange is an important process of water-rock interaction that obviously influences the major ion composition of groundwater (Xiao et al., 2012). Although the cation exchange is widespread in geochemical evolution of all groundwater, it is essential to know and identify the various changes undergone by water during their traveling processes in groundwater system under the influence of anthropogenic activities. In the present study, molar Na/Ca ratio changes between 0.5 and 106.09 with an average of 3.80, suggesting the presence of Na⁺ and Ca²⁺ exchange. It could be conveyed as the following reaction:



Where X is sites of cation exchange.

Schoeller proposed that chloro-alkaline indices could be used to study the cation exchange between the groundwater and its host environment during residence or travel (Schoeller, 1965; Marghade et al., 2012; Li et al., 2013). The Schoeller indices, such as CAI-I and CAI-II, are calculated by the following equations, where all ions are expressed in meq/L:

$$\text{CAI - I} = \frac{\text{Cl}^- - (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (1)$$

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

When the Schoeller indices are negative, an exchange of Ca²⁺ or Mg²⁺ in groundwater with Na⁺ or K⁺ in aquifer materials takes place, Ca²⁺ or Mg²⁺ will be removed from solution, and Na⁺ or K⁺ will be released into the groundwater. At the same time, negative value indicates chloro-alkaline disequilibrium and the reaction is

known as cation-anion exchange reaction. During this process, the host rocks are the primary sources of dissolved solids in the water. In another case, if the positive values are obtained, then the inverse reaction possibly occurs and it is known as base exchange reaction. In the present study, almost all groundwater samples had negative Schoeller index values (Supplement Table S1), which indicates cation-anion exchange (chloro-alkaline disequilibrium). The results show clearly that Na^+ or K^+ is released by Ca^{2+} or Mg^{2+} exchange indeed, which is a common form of cation-exchange in the study area. This also further confirms that the cation exchange is one of the major contributors for higher concentration of Na^+ in the groundwater and it is still an important geochemical process of groundwater in Subei lake basin under the influence of human activities.

5.2 The formation mechanisms of groundwater and surface water

The saturation index is one of vital geochemical parameters in hydrogeology and geochemistry field, which is usually useful for identifying the existence of some common minerals in the groundwater system (Deutsch, 1997). In this present study, saturation indices (SI) with respect to gypsum, anhydrite, calcite, dolomite, aragonite and halite were calculated in terms of the following equation (Lloyd and Heathcote, 1985):

$$\text{SI} = \log \left(\frac{\text{IAP}}{k_s(T)} \right) \quad (3)$$

Where IAP is the relevant ion activity product, which could be calculated by multiplying the ion activity coefficient γ_i and the composition concentration m_i , and $k_s(T)$ is the equilibrium constant of the reaction considered at the sample temperature. The geochemical computer model PHREEQC (Parkhurst and Appelo, 2004) was used to calculate the saturation indices. When the groundwater is saturated with some mineral, SI equals zero; positive values of SI represent oversaturation, and negative values show undersaturation (Appelo and Postma, 1994; Drever, 1997).

Figure 10 indicates the plots of SI versus the total dissolved solids (TDS) for all the groundwater samples. The modeled values of SI for anhydrite, gypsum and halite oscillate between -5.27 and -1.11, -4.8 and -0.65, -8.61 and -5.9 with averages

-2.62,-2.16,-7.49, respectively. It shows that the groundwater in study area was below the equilibrium with anhydrite, gypsum and halite, indicating that these minerals are anticipated to dissolve. However, the SI of aragonite, calcite, and dolomite range from -0.74 to 1.09, -0.59 to 1.25, and -1.16 to 2.64 with averages 0.32, 0.48, and 0.81, respectively. On the whole, the groundwater samples were dynamically saturated to oversaturated with aragonite, calcite and dolomite, representing that the three major carbonate minerals may have affected the chemical composition of groundwater in Subei lake basin. The results show that the groundwater may well produce the precipitation of aragonite, calcite and dolomite. Saturation of aragonite, calcite and dolomite could be attained quickly due to the existence of abundant carbonate minerals in the groundwater system.

The soluble ions in natural waters mainly derive from the rock and soil weathering (Lasaga et al., 1994), anthropogenic input, and partly from the precipitation input. In order to make an analysis of the formation mechanisms of hydrochemistry, Gibbs diagrams have been widely used in hydrogeochemical studies (Feth and Gibbs, 1971;Naseem et al., 2010;Marghade et al., 2012;Yang et al., 2012b;Xing et al., 2013). Gibbs (1970) recommended two diagrams to assess dominant effects of precipitation, rock weathering, or evaporation on geochemical evolution of groundwater in semi-arid and arid regions. The diagrams show the weight ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ against TDS, and precipitation dominance, rock dominance, and evaporation dominance are included in the controlling mechanisms (Gibbs, 1970). The distributed characteristic of samples in Fig.11 shows that rock weathering is the dominant mechanism in the geochemical evolution of the groundwater in the study area. The ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ was mostly less than 0.5 in shallow and deep Cretaceous groundwater, with low TDS values (Fig.11). It shows that rock weathering was the main mechanism controlling the chemical compositions of shallow and deep Cretaceous groundwater. In the Quaternary groundwater, about 2/3 of samples had the ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ greater than 0.5 and higher TDS between 314 and 1202 mg/L, which indicated that the Quaternary groundwater was not only controlled by rock weathering, but also by

evaporation-crystallization process. It is obvious that the weight ratio of Na^+ / $(\text{Na}^+ + \text{Ca}^{2+})$ spreads from low to high without great variation of TDS, which indicated that cation exchange also played a role by increasing Na^+ and decreasing Ca^{2+} under the background of rock dominance. During the cation exchange process, the TDS values do not change obviously because 2 mmol/L of Na^+ is released by 1 mmol/L Ca^{2+} exchange, and the weight of 1 mmol/L of Ca^{2+} (40mg/L) is nearly equal to that of 2 mmol/L of Na^+ (46 mg/L).

In August, the average isotopic values of deep Cretaceous groundwater ($\delta^{18}\text{O}$: -8.4‰, δD : -67‰) were enriched compared with the Quaternary groundwater ($\delta^{18}\text{O}$: -8.8‰, δD : -71‰), but in December, the average isotopic values of deep Cretaceous groundwater ($\delta^{18}\text{O}$: -8.5‰, δD : -66‰) were depleted compared with the Quaternary groundwater ($\delta^{18}\text{O}$: -8.2‰, δD : -65‰), the stable isotopic values of Quaternary groundwater had a wider range from August to December than those of deep Cretaceous groundwater. This may be explained by heavy isotope enrichment in the Quaternary groundwater caused by evaporation given that there was no effective precipitation in the study area during the period from August to December; meanwhile, the deep Cretaceous groundwater may be mainly recharged by lateral inflow from groundwater outside the study area, which resulted in smaller seasonal fluctuations in the isotopic values.

Furthermore, the average values of $\delta^{18}\text{O}$ and δD of the shallow Cretaceous groundwater are -8.3 and -66‰, -8.2 and -64‰, respectively in August and December; meanwhile, the average values of $\delta^{18}\text{O}$ and δD of the deep Cretaceous groundwater are -8.4 and -67‰, -8.5 and -66‰, respectively in August and December. Thus, given the precision of the analysis, shallow Cretaceous groundwater and deep Cretaceous groundwater have similar isotopic characteristics in Subei lake basin, which indicates that they may be replenished by the similar water source due to the similar geological setting. This also validates the existence of leakage. The similar isotopic characteristic of groundwater from the Cretaceous aquifer may be ascribed to the increasingly close relationship between shallow Cretaceous groundwater and deep Cretaceous groundwater due to changes in hydrodynamic field caused by intensive groundwater

exploitation. Conversely, the phenomenon that the deep groundwater is depleted in heavy isotopes compared with the shallow groundwater was found in Habor lake basin located in recharge area (Yin et al., 2009).

The hydrogen and oxygen isotopes signatures in lake water show that lake water contains abnormally high levels of heavy isotopic composition. Compared with the stable isotopic values in groundwater, it is evident that lake water has undergone a greater degree of enrichment in heavy isotopes, which further illustrates that fractionation by strong evaporation is occurring predominantly in the lake water. This also proves to be in accordance with the unique hydrochemical characteristics of lake water. In addition, the slope and intercept of the regression line for $\delta^{18}\text{O}$ and δD in lake water were 1.47, -29.09, lower than the slope and intercept (7.51, -7.12) observed for lake water in Habor lake basin (Yin et al., 2009). By comparison, it is clearly confirmed that lake water in discharge area has undergone stronger evaporation than lake water in recharge area. As a result, lake water in Subei lake basin contains more heavily isotopic composition than that in Habor lake basin.

6. Conclusions

The present study examines the hydrochemical and isotopic composition of the groundwater and surface water in Subei lake basin with various methods such as correlation analysis, saturation index, Piper diagram and Gibbs diagrams. The combination of major elements geochemistry and stable isotopes ($\delta^{18}\text{O}$, δD) has provided a comprehensive understanding of the hydrodynamic functioning and the processes of mineralization that underpin the geochemical evolution of the whole water system. The hydrochemical data show that three groups of groundwater are present in Subei lake basin: the Quaternary groundwater, shallow Cretaceous groundwater and deep Cretaceous groundwater. The analysis of groundwater chemistry clarifies that the chemistry of lake water was controlled by strong evaporation and recharge from overland flow and groundwater; meanwhile the major geochemical processes responsible for the observed chemical composition in groundwater are the dissolution/precipitation of anhydrite, gypsum, halite and calcite,

the feldspar and dolomite weathering. Furthermore, the cation exchange has also played an extremely vital role in the groundwater evolution. The absolute predominance of rock weathering in the geochemical evolution of groundwater in the study area is confirmed by the analytical results of Gibbs diagrams. The stable isotopic data indicate that groundwater is of modern local meteoric origin rather than the recharge from precipitation in paleo-climate conditions. Unlike significant difference in isotopic values between shallow groundwater and deep groundwater in Habor lake basin, shallow Cretaceous groundwater and deep Cretaceous groundwater have similar isotopic characteristics in Subei lake basin. Due to evaporation effect and dry climatic conditions, heavy isotopes are more enriched in lake water than groundwater. The low slope of the regression line of $\delta^{18}\text{O}$ and δD in lake water could be ascribed to a combination of mixing and evaporation under conditions of low humidity. By comparison of the regression line for $\delta^{18}\text{O}$ and δD , lake water in Subei lake basin contains more heavily isotopic composition than that in Habor lake basin, indicating that lake water in discharge area has undergone stronger evaporation than lake water in recharge area.

Much more accurate groundwater information has been obtained by conducting this study on Subei lake basin, which will further enhance the knowledge of geochemical evolution of groundwater system in the whole Ordos basin and gain comprehensive understanding of Subei lake basin typical of lake basins in discharge area where significant changes in groundwater system have taken place under the influence of human activity. More importantly, it could provide valuable groundwater information for decision makers and researchers to formulate scientifically reasonable groundwater resources management strategies in these lake basins of Ordos basin so as to minimize the negative impacts of anthropogenic activities on the water system. In addition, given that there have been a series of ecological environment problems, more eco-hydrological studies in these lake basins are urgently needed to do from the view of sustainable development of natural resources environment in the future.

Acknowledgements This research was supported by the State Basic Research Development Program (973 Program) of China (Grant No. 2010CB428805) and the

International Green Peace Organization. The authors are grateful for our colleagues for their assistance in sample collection and analysis. Special thanks go to the editor and the two anonymous reviewers for their critical reviews and valuable suggestions.

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Table 1 The chemical composition and isotopic data of lake water in August and December 2013.

ID	Date	EC ($\mu\text{S}/\text{cm}$)	T ($^{\circ}\text{C}$)	pH	DO (mg/L)	ORP (mV)	K ⁺ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	CO ₃ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	TDS (mg/L)	δD (‰)	$\delta^{18}\text{O}$ (‰)
EEDS08	29-Aug-2013	130 400	22.5	10.11	11.06	-1.8	1956	42 020	2.28	3.01	37 440.28	22 066.83	6000.3	19 356.45	98.93	125 943.93	-1	19.4
EEDS09	29-Aug-2013	190 100	24.3	10.25	15.8	-14.8	6475	96 530	0.00	2.4	108 517.4	37 581.86	12 661.65	46 565.53	511.48	302 514.49	15	29.4
EEDS38	30-Aug-2013	1017	23.7	8.86	7.65	61.8	10.63	97.59	17.21	70.03	32.71	92.85	480.68	0	1.07	562.43	-45	-5.8
EEDS08	6-Dec-2013	120 400	1.8	8.9		17.6	1997.73	36 617.7	11.52	3.7	30 787.74	7513.4	5186.7	19 406.47	87.48	99 019.09	-18	5.8
EEDS09	6-Dec-2013	229 000	2.3	8.49		39.5	7567	77 840	36.34	11.39	113 003.44	5276.76	11 593.8	13 754.59	207.99	223 494.4	-9	16.2
EEDS38	4-Dec-2013	4200	1.1	10.47	17.96	26.3	38.88	602	9.06	352.2	164.54	448.23	1423.8	900.3	9.53	3236.64	-28	-2.6
EEDS60	4-Dec-2013	14 080	2.7	9.04	10.58	23.6	56.154	3393.74	4.27	41.49	1418.76	386.04	1067.85	2600.87	11.77	8447.02	-28	-1.9

Table 2 Correlation coefficient of major parameters in groundwater

	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	pH
K ⁺	1.000	0.538	0.309	0.560	0.553	0.300	0.572	0.534	-0.063
Na ⁺		1.000	0.217	0.651	0.824	0.485	0.602	0.728	-0.072
Ca ²⁺			1.000	0.754	0.375	0.665	0.478	0.796	-0.600
Mg ²⁺				1.000	0.655	0.819	0.582	0.939	-0.382
Cl ⁻					1.000	0.375	0.576	0.776	-0.144
SO ₄ ²⁻						1.000	0.160	0.770	-0.226
HCO ₃ ⁻							1.000	0.625	-0.398
TDS								1.000	-0.378
pH									1.000

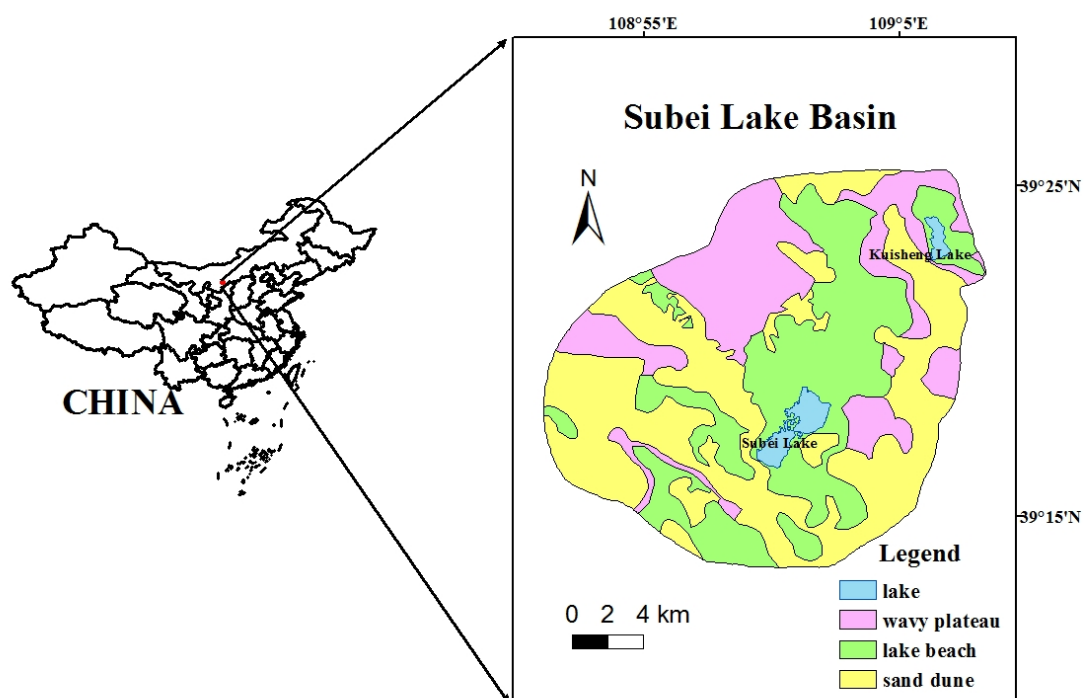


Fig.1 Location of the study area and geomorphic map

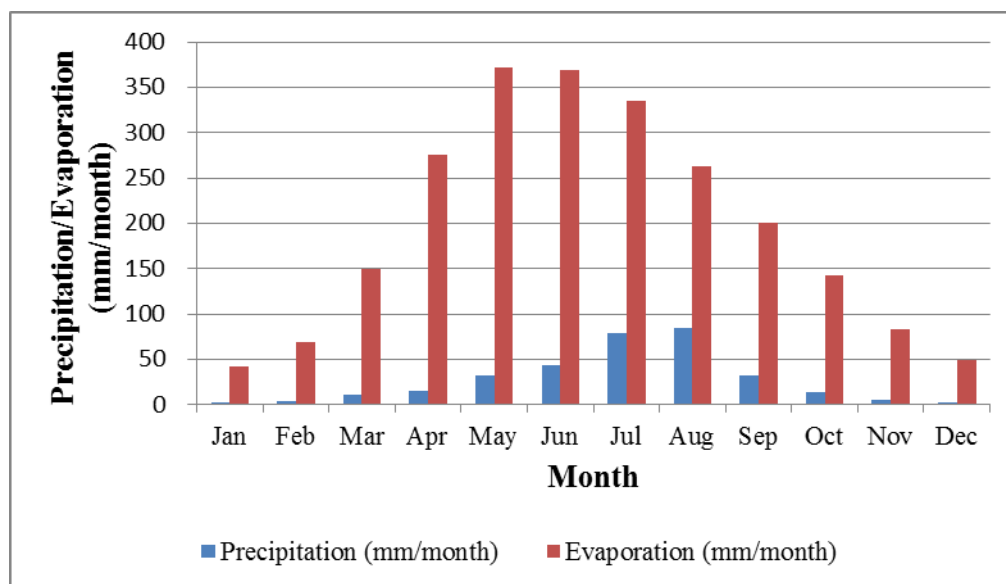


Fig.2 Average monthly precipitation and evaporation in the study area

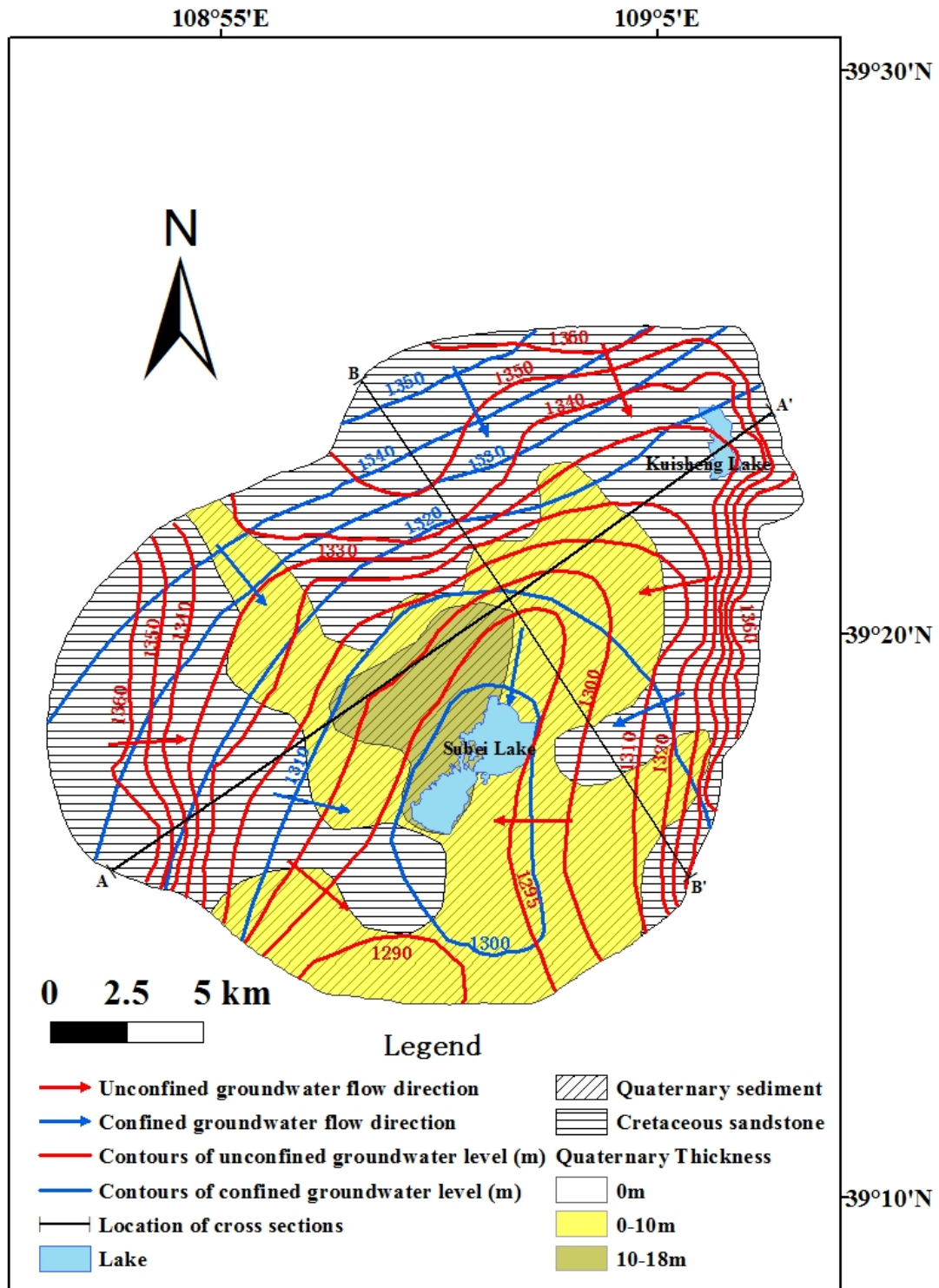


Fig.3 Hydrogeological map of the study area. Data source: revised from original source (Inner Mongolia Second Hydrogeology Engineering Geological Prospecting Institute, 2010).

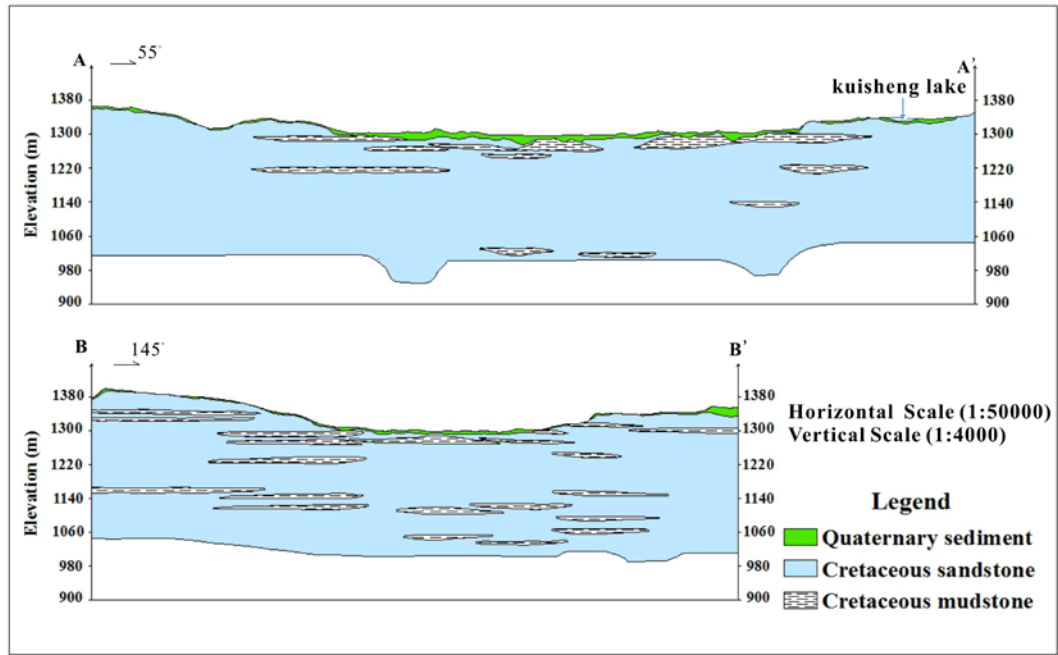


Fig.4 Geologic sections of the study area. Data source: revised from original source (Inner Mongolia Second Hydrogeology Engineering Geological Prospecting Institute, 2010).

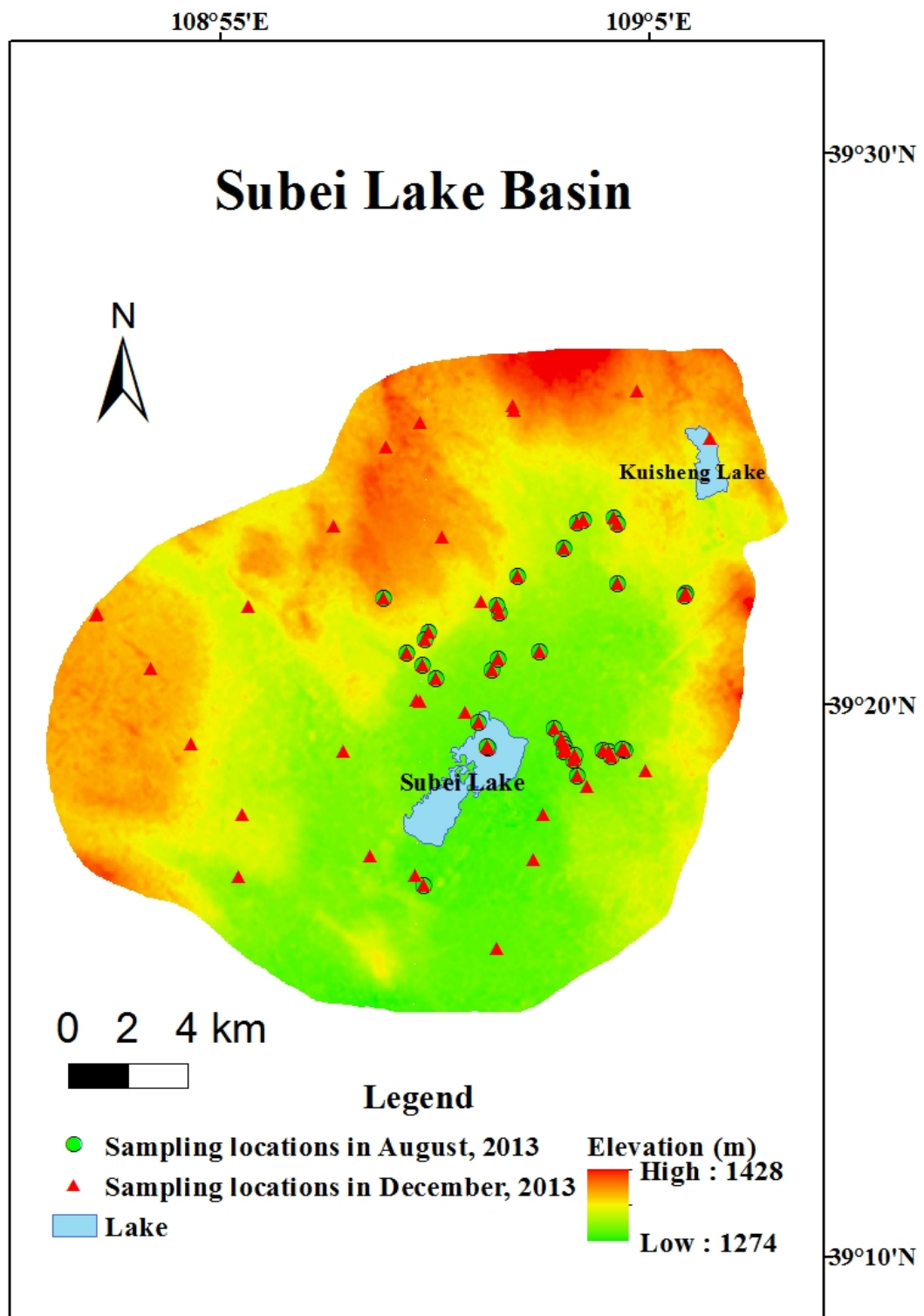


Fig.5 Sampling locations in August and December, 2013.

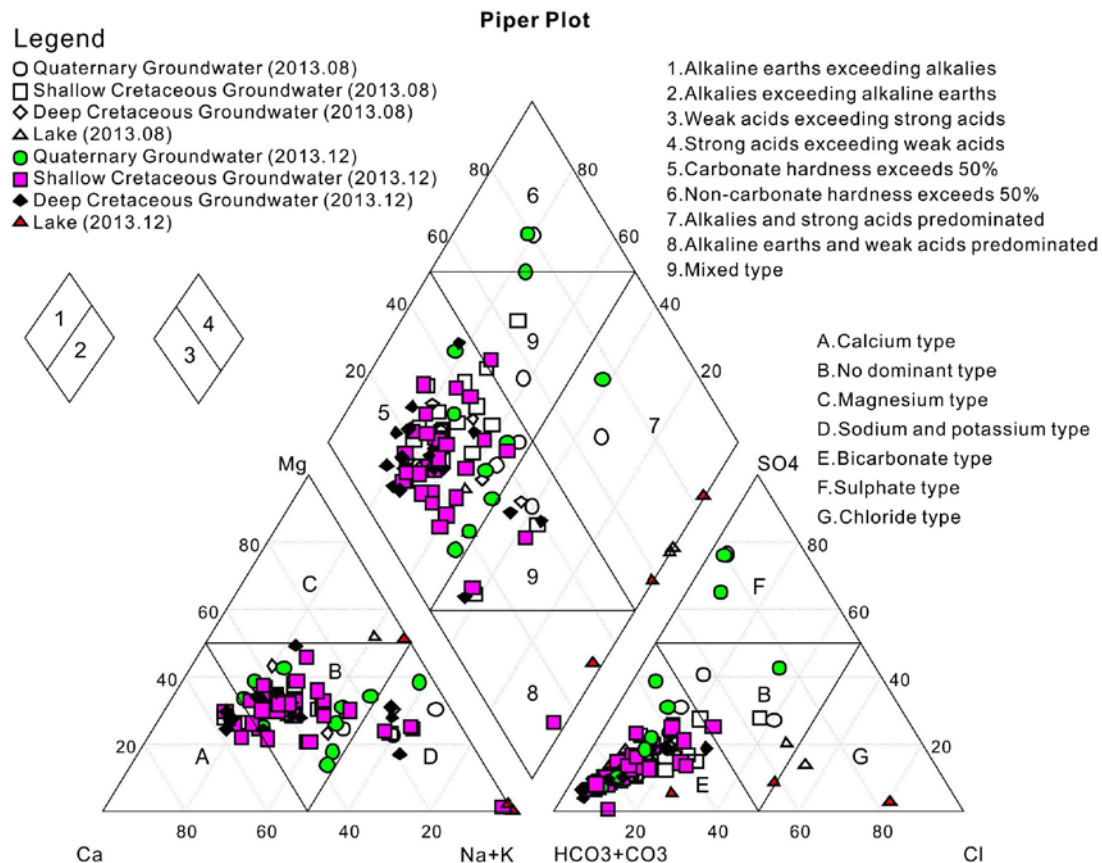


Fig.6 Piper diagram of groundwater and lake water in August and December, 2013.

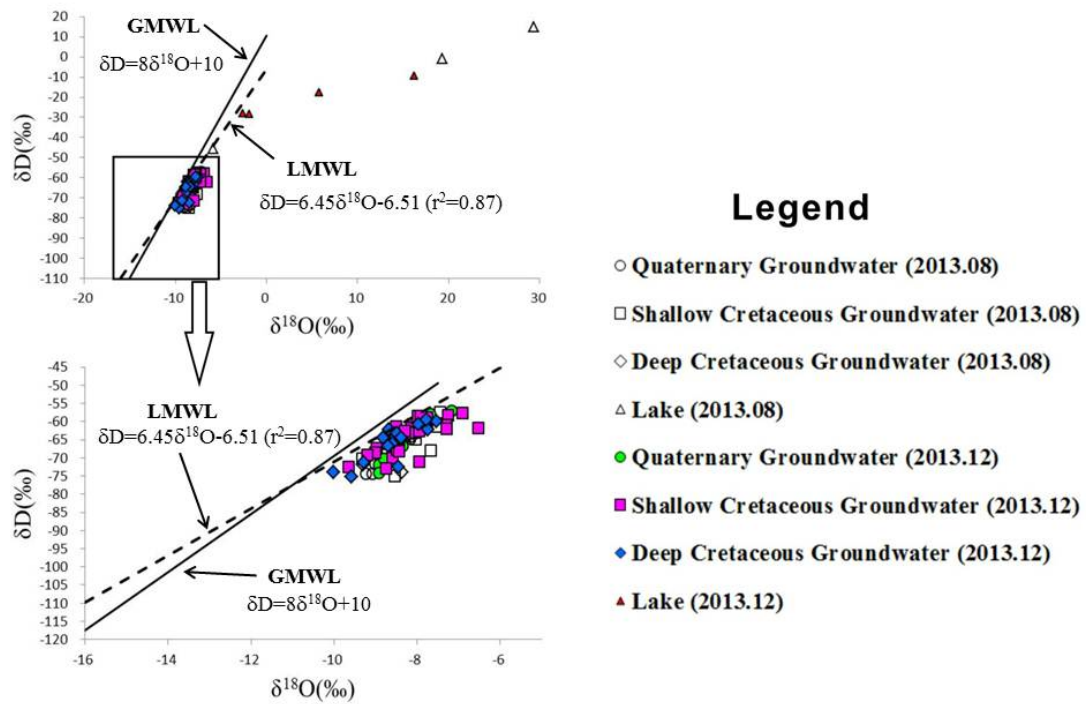


Fig.7 Relationship between hydrogen and oxygen isotopes in groundwater and lake water in August and December, 2013.

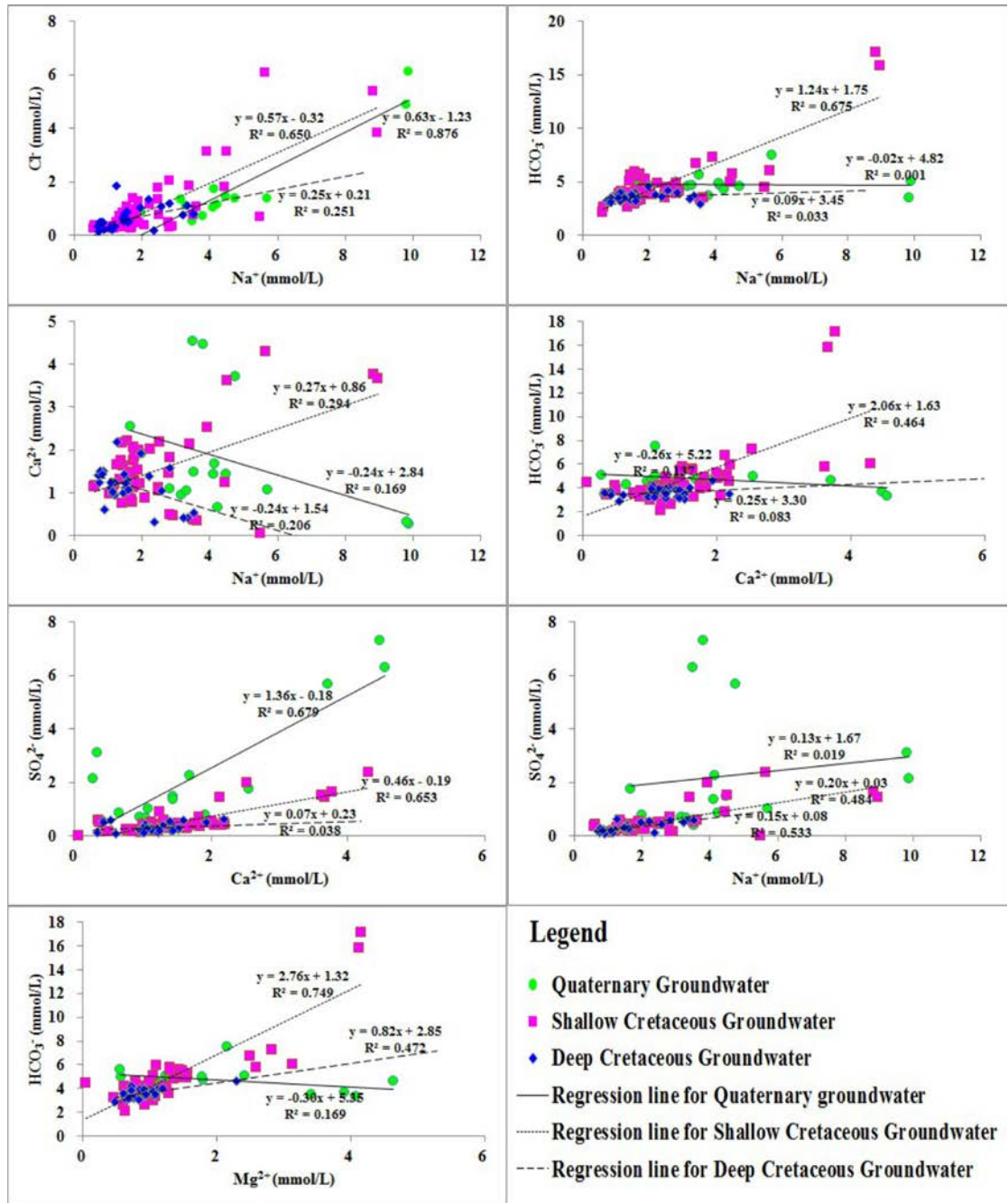


Fig.8 Relationship between some pairs of ions in groundwater.

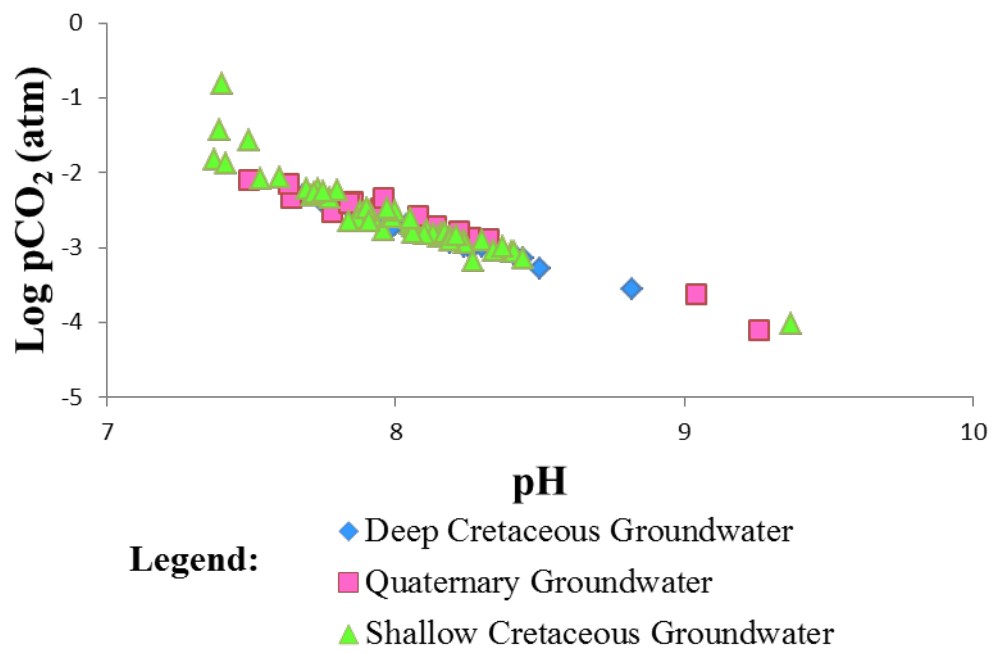
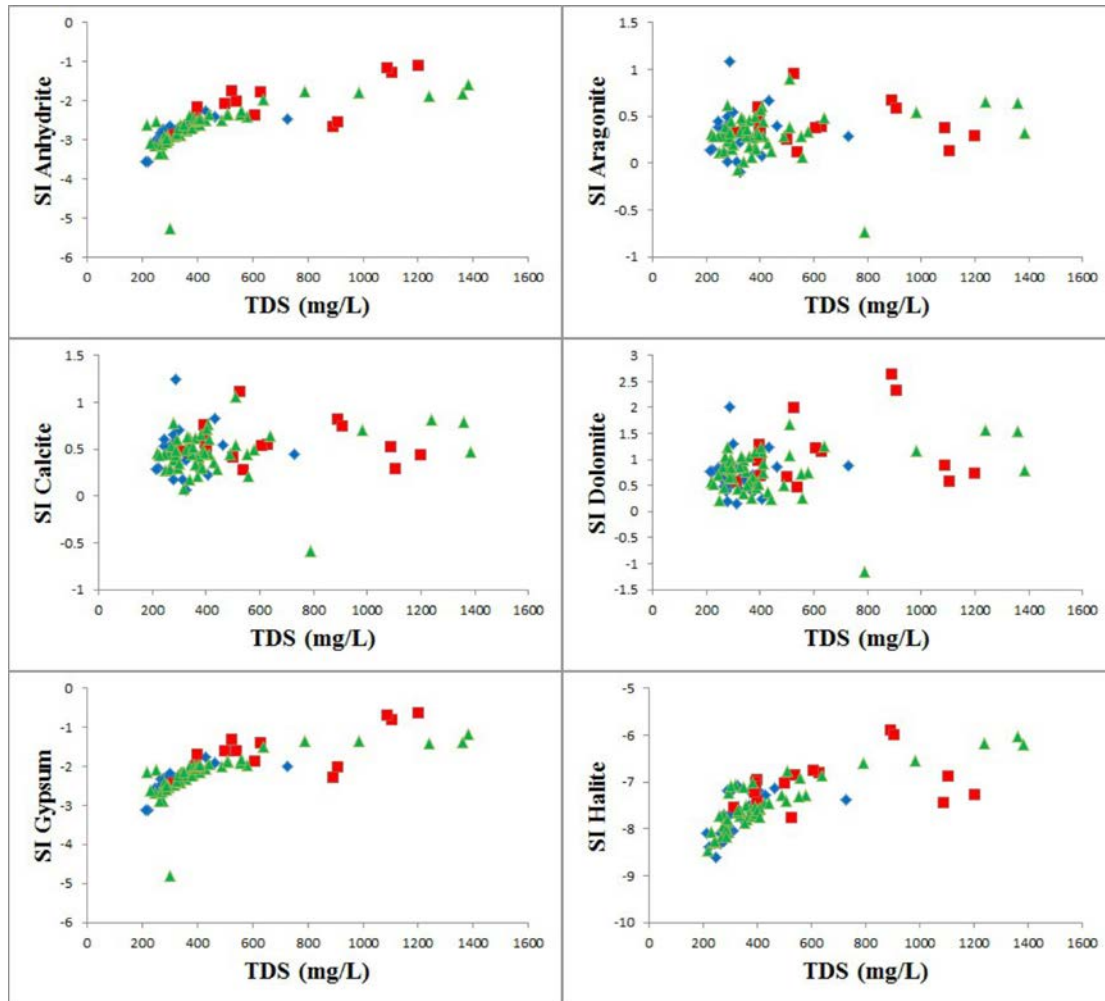


Fig.9 Geochemical relationship of pH vs. Log (pCO₂) in groundwater.



◆ Deep Cretaceous Groundwater
Legend: ■ Quaternary Groundwater
 ▲ Shallow Cretaceous Groundwater

Fig.10 Plots of saturation indices with respect to some minerals in groundwater.

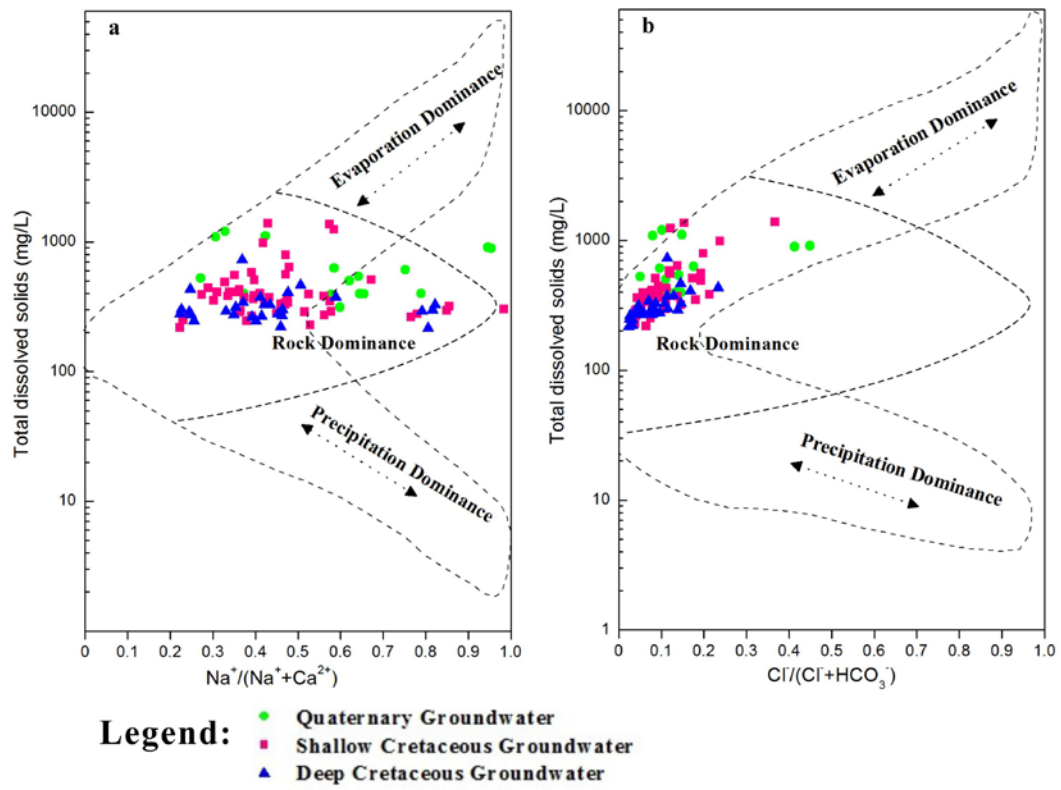


Fig.11 Gibbs diagram of groundwater samples in Subei lake basin: (a) TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$, (b) TDS vs. $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$.