Groundwater recharge and evolution in the Dunhuang Basin, northwestern China

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Abstract

Groundwater recharge and evolution in the Quaternary aquifer beneath the Dunhuang Basin was investigated using chemical indicators, stable isotopes, and radiocarbon data to provide guidance for regional water management. The quality of groundwater and surface water is generally good with low salinity and it is unpolluted. The dissolution of halite and sylvite from fine-grained sediments controls concentrations of Na⁺ and K⁺ in the groundwater, but Na⁺/Cl⁻ molar ratios > 1 in all samples are also indicative of weathering of feldspar contributing to excess Na⁺. The dissolution of carbonate minerals yields Ca²⁺ to the groundwater, thereby exerting a strong influence on groundwater salinity. The δ¹⁸O and δ²H values in unconfined groundwater are enriched along the groundwater flow path from SW to NE. In contrast, confined groundwater was depleted in heavy isotopes, with mean values of −10.4%, δ¹⁸O and −74.4%, δ²H. Compared with the precipitation values, all of the groundwater samples were strongly depleted in heavy isotopes, indicating that modern direct recharge to the groundwater aquifers in the plains area is quite limited. The unconfined water is generally young with radiocarbon values of 64.9–79.6 pmc. In the northern basin, radiocarbon content in the confined groundwater is less than 15 pmc and an uncorrected age of ~15 ka, indicates that this groundwater was recharged during a humid climatic phases of the late Pleistocene or early Holocene. The results have important implications for inter-basin water allocation programmes and groundwater management in the Dunhuang Basin.

1. Introduction

Water demand for agricultural, household and environmental uses is rapidly rising due to continuously increasing population especially in the developing world, and more and more areas are expected to experience imbalance of supply and demand for water in the near future (Vairavamoorthy et al., 2008). Furthermore, climate change, population growth, and economic development will likely affect the future availability of water resources in arid and semi-arid regions. One of the main issues of these areas that is affected by climate change is the quality and quantity of the water resources that are supplied to the growing population. Increasing population density, economic activity, and unsustainable water management practices have led to over-exploitation of many of the more easily accessible freshwater resources around the globe (Vörösmarty et al., 2010). Many of the world’s largest rivers such as the Nile, Colorado, Yellow river, Indus and Ganges no longer reach the sea for part of the year (Conway and Hulme, 1993; Shiklomanov, 1997; Archer, 2003; Christensen et al., 2004; Liu and Jun, 2004; Conway, 2005). In sub-humid to arid areas, the total global groundwater depletion has increased from 126 km³ a⁻¹ in 1960 to 283 km³ a⁻¹ in 2000 due to increased groundwater abstraction, especially in the world’s major agricultural regions, including NW India, north China, and the central USA (Wada et al., 2010). These regions are water-stressed and the anticipated climatic trends for the near future further threaten this precarious situation (Gleick et al., 2006; Bates et al., 2008). Alcamo et al. (2000) found that the areas affected by severe water stress will expand and intensify, growing globally from 36.4 to 38.6 million km² between 1995 and 2025. Some cities in the drier parts of the world are likely to have exhausted their groundwater reserves in little more than a decade. Water scarcity has brought into focus the urgent need for planned action to manage water resources effectively as it is widely acknowledged that water is a major limiting factor in the socio-economic development of a world with a rapidly expanding population. Sustainable management of water resources to meet human and ecosystem needs will require accurate estimates of groundwater recharge, as the surface water resources are generally scarce and highly unstable in semiarid and arid regions, with the result that groundwater is the primary source of water in these regions (Kinzelbach et al., 2003; Scanlon et al., 2006).

Situated deep in the hinterland of Eurasia, China’s northwestern inland zone has a very arid climate. The landscape in these regions is fragile due to the low and irregular precipitation, high temperatures and evaporation, and notable drought periods (Ma et al., 2005). In such arid and semi-arid environments, groundwater is not only an important source of public water supply, but is also...
important to the regional ecology. Since the 1950s, human activities, and particularly the exploitation of land and water resources associated with dramatic population growth, have led to great changes in the water regime and have created serious environmental consequences, including declines in the regional groundwater levels, desertification, and drying of rivers and lakes in the lower reaches of river basins (Feng et al., 2005; Zhang, 2005; Chen et al., 2010; Li, 2010; Huang and Pang, 2010). For example, the groundwater level has dropped widely by as much as 35 m in the Minqin Basin since the 1960s (Ma et al., 2005). In the lower Tarim River, runoff has ceased to flow into the 350 km long river since the construction of the Daxihai Water Reservoir in 1972, causing severe damage to the riparian forest dominated by Populus euphratica (Song et al., 2000). The so-called “Green Corridor” and the highway along the Lower Tarim River (Kuala to Ruqiuang, part of National Highway G218) are endangered by degrading riparian vegetation and desertification (Huang and Pang, 2010). Desertification in the Shule River Basin is also a very severe problem. The sand dune along the Shule River has evolved from immobile dunes to mobile dunes because of the degeneration of the vegetation cover (Ding et al., 2001). If this situation continues, further deterioration of the environment and ecosystems of this vast area is unavoidable (Zhu et al., 2008). Careful studies of the characteristics of the groundwater and its evolution under natural water circulation processes help to provide scientific guidelines for sustainable exploitation of the region’s water resources and prevention of further degradation of the regional environment.

In recent years, the Chinese government and scientists have carried out many studies to assess the characteristics and utilization of the groundwater resources in northwestern China’s arid regions. Most of the research has taken place in the eastern and middle parts of the Hexi Corridor (i.e., the Zhangye, Ejina, and Minqin Basins), with important results that provide guidance for regional water management. For example, the deep groundwater of the Minqin Basin was recharged under cool and wet conditions during the late Pleistocene to Holocene periods based on an analysis of isotopic, noble gas, and chemical indicators (Ma et al., 2005; Edmunds et al., 2006; Zhu et al., 2008). Some authors have studied the hydro-geochemical evolution and residence time of water along the groundwater flow path in the Zhangye and Ejina Basins (Feng et al., 2005; Chen et al., 2006). The exchanges between groundwater and surface water in the Zhangye Basin have also been examined, using either a 3D groundwater flow simulation model or Ra analysis (Wu et al., 2004; Hu et al., 2007). As yet, similar studies have not been performed in the western part of the Hexi Corridor, Dunhuang Basin is a type locality of this area, and Dunhuang was an important city on the ancient Silk Road, and now is a renowned tourist city famous for the Mogao Caves, Crescent Lake and Mingsha Shan (literally, Echoing-Sand Mountain in the Kumtag Desert). However, increasing attention has been paid to Dunhuang recently because its famed Crescent Lake has been rapidly shrinking into the desert sand due to groundwater depletion (Yardley, 2005; Jiao, 2010), and because of the inter-basin water allocation programme in the Shule River catchment including Dunhuang Basin. Crescent Lake has dropped more than 7.5 m in the past three decades, while the groundwater table elsewhere in the basin has fallen by as much as 10 m, and the central government has indicated a national priority to rehabilitate this important and historic area. However, characteristics of groundwater beneath Dunhuang Basin remain poorly understood (Piao et al., 2003). It is certain that increasing surface water in the basin will increase the groundwater recharge.

The main objective of this study is to present the results from a wide selection of geochemical and isotopic indicators revealing the main characteristics of the groundwater in the Dunhuang Basin. The specific goals included: (1) using stable environmental isotopes (\(^{18}O\), \(^{2}H\) and \(^{14}C\)) to determine the evolution and age of the groundwater under natural conditions; (2) using the chemistry of major ions to determine the dominant geochemical processes that take place along the groundwater flow paths. The results of this study will not only improve understanding of the groundwater system in the whole Hexi Corridor, but will also provide essential information and a theoretical basis for the design of effective water resources management in the Dunhuang Basin.

2. The study area

2.1. General setting

Dunhuang, located at the western end of the Hexi Corridor in northwestern China’s Gansu Province, was an important town on the ancient Silk Road (Fig. 1). The basin lies between the Mingsha Shan (Echoing-Sand Mountain in the Kumtag Desert) and Sanwei Mountains in the SE and the Mazong Mountains in the north, and spreads into the Gobi desert in the west (Fig. 2). The basin has a drainage area of 6290.8 km², but the actual area covered by groundwater is much smaller, approximating 1400 km². The oasis consists of two major irrigation districts, with a total irrigation area of 298 km². The Nanhui Irrigation District, which is about 60 km SW of Dunhuang City, is a zonal basin that spreads from the Sanwei Mountains in the SE to the Gobi desert in the NW. The altitude ranges between 1150 and 1200 m. The surrounding hills, combined with well-developed ravines, produce floods during each rainfall event. There are many spring-fed reservoirs in this area. The Dunhuang Irrigation District, with an elevation ranging from 800 to 1500 m, stretches from the Mingsha Shan in the SW to Xihu in the NE, and contains Dunhuang City, the administrative heart of the region (Fig. 1).

The climate is continental, with great variation in temperature and precipitation during the year. The temperature ranges from -28 °C to 44.1 °C, with a diurnal temperature range of up to 30 °C. The average yearly rainfall is <40 mm (Jiao, 2010). In the extreme drought year of 1956, precipitation was only 6.4 mm. Most of the rainfall appears as summer rainstorms, and these storms have historically caused severe flooding. The potential annual evapotranspiration is around 2400 mm (Jiao, 2010), with the highest evaporation intensity in May and June. Because of the sparse and highly variable precipitation, runoff from the mountains produces no perennial streams that reach the plains. The total amount of surface water resources is about 454 million m³ from the Danghe River and some temporary rivers that flow through ravines after a storm. The Danghe River originates in the Qilian Mountains, south of the study area, and is recharged by melting of glaciers and snow, springs, and rainfall. The meltwater accounts for nearly 39.8% of the total runoff (Chen and Qu, 1992). The Danghe Reservoir, at the southern end of the basin, has been a significant barrier to surface flow into the Dunhuang Basin since it was built in 1975. The precipitation that falls in the Sanwei Mountains produces some seasonal streams, which accumulate and run into the valleys of Cuimutu, Duoba, Dongshui, and Xishui, forming a total runoff of approximately 40 million m³ a\(^{-1}\).

2.2. Geology and hydrogeology

From the late Tertiary, especially from the end of the Pleistocene and the beginning of the early Pleistocene, intensive denudation and erosion from the Qilian mountains led to significant transfer of clastic material to the basin depressions. During the Quaternary, the Sanwei Mountains began to rise rapidly (Zhang and Liu, 1985), which brought much of the clastic material into the basin, forming the thick Quaternary aquifer of diluvial and alluvial sediments, and some aeolian and lacustrine deposits. The impermeable basement
rocks of the study area consist of conglomerate, argillaceous sandstone, and muddy siltstone that formed during the Tertiary, and these materials were cemented by calcareous mud.

The main aquifers that overlie this basement material are composed of diluvial and alluvial sediments carried into the area by the Danghe River, the Shule River, and some small seasonal rivers, and there are lacustrine deposits in some low-lying areas. Unconsolidated Quaternary sediments that reach thicknesses of hundreds of meters were deposited in the southern foreland; and reach thicknesses of tens of meters at the edge of the basin. Together, these sediments form significant unconfined and confined groundwater systems. In the western part of the Dunhuang Irrigation District and near the urban area, the alluvial and diluvial aquifer is formed of highly permeable cobbles, gravels, and sands ranging from 200 to 400 m in thickness. The aquifer system is unconfined, with the water level 10–50 m below the surface (Gansu Geology Survey, 1978). The single-well water yield can be greater than 1000 m$^3$ day$^{-1}$. Spreading north of Dunhuang City, the aquifer changes to inter-bedded sands and gravels, with a groundwater depth of 3–10 m, and the single-well water yield ranges between 100 and 1000 m$^3$ day$^{-1}$. At the northern and eastern edges of the alluvial fans, the aquifer comprises inter-bedded fine sands and clays, and becomes confined or semi-confined, with piezometric levels of less than 3 m. As a result, groundwater is lost rapidly by the region’s intense evaporation. In some places, the groundwater emerges from springs to form low-lying puddles. The overall groundwater flow is generally from the SE to the NW (Fig. 3). In 1967, there were only 400 wells, with an annual groundwater exploitation of about $0.1 \times 10^9$ m$^3$ a$^{-1}$, but after 2002, the number of wells had increased to more than 1460 and groundwater abstraction had reached $0.6 \times 10^9$ m$^3$ a$^{-1}$. Undoubtedly the groundwater is being extracted much more rapidly than it is being replaced, since groundwater levels have declined at rates as high as 0.3–0.4 m a$^{-1}$ since the 1960s.

2.3. Inter-basin water allocation program

In order to resolve the water scarcity in the Dunhuang area, the National Development and Reform Commission and Ministry of Water Resources have carried out a series of works since 2008 and finally the ‘Dunhuang Water Resources Rational Utilization and Ecological Protection Planning’ was announced in 2010. This programme will focus on the goal of governance, ecological construction and environmental protection, and special planning of water resource in Dunhuang region. This project was started in 2011 with work mainly focusing on establishing rational water rights, reforming irrigation water use as well as restoring the Crescent Lake. As part of a major programme, 88 million m$^3$ a$^{-1}$ surface water will be diverted to Dunhuang along a 202 km aqueduct from the Sugan Lake water system, of which 40 million m$^3$ is to be used for rehabilitation of the Crescent Lake (Gansu Water Management Bureau, 2011).

3. Materials and methods

To obtain sufficient data to cover the study area, field work was carried out during most of a year, from July 2010 to June 2011. A
total of 25 representative samples were obtained, including four surface water samples from the Danghe Reservoir and the main channel of the Danghe River (covering the region from the upper to lower reaches), and 19 groundwater samples from water supply and irrigation boreholes as well as from springs within the Quaternary aquifer across the study area. To examine the different recharge pathways of the aquifers, a fracture water sample was also collected from the southern Sanwei Mountains and two groundwater samples were extracted from the western Guazhou district. Prior to the sampling, all boreholes had been pumped continuously for at least 2 months.

Water temperature, specific electrical conductivity (SEC), pH and total dissolved solids (TDS) were measured in the field using a sensION156 portable multi-parameter meter (Hach, Loveland, CO), and the total alkalinity (as HCO\textsubscript{3}) was determined using a Model 16900 digital titrator (Hach) with a bromocresol green-
methyl red indicator system, with a precision of ±1% (SD). All samples were filtered through a 0.45-μm membrane filter, divided into two subsamples, and stored in acid-washed, well-rinsed, low-density-polyethylene bottles for subsequent analysis. The subsample used to determine cations was acidified with 1% HNO₃, to a pH of around 1.5 to stabilize the metals. The subsample used to determine anions and the stable isotopes was not acidified. Unfiltered 1.5-L samples were collected for the radiocarbon (14C) analysis.

Major ion contents were analyzed by means of ion chromatography using an ICS-2500 ion chromatograph (Dionex, Sunnyvale, CA), with an analytical precision of 3% of the concentration based on the reproducibility of repeated analysis of the samples. The detection limit was 0.01 mg L⁻¹. Water O and H isotope ratios (δ²H, δ¹⁸O) were measured using off-axis integrated-cavity-output laser spectroscopy (Model DLT-100, Los Gatos Research, Inc., Mountain View, CA). In this analysis, each sample was measured six times and the first two values were discarded; based on the remaining four measurements, the precision was 0.2% for ¹⁸O/¹⁶O and 0.6% for δ²H. All measured values are reported relative to Vienna Standard Mean Ocean Water (VSMOW). Chemical and isotope analyses were carried out at the Key Laboratory of Western China’s Environmental System (Ministry of Education), Lanzhou University. All of the chemical data was validated using the ion balance method, and had a precision within 5%.

Radiocarbon samples were measured at the CSIRO Land and Water Laboratory, Adelaide, South Australia. Dissolved inorganic C (DIC) was reacted with 85% phosphoric acid to produce CO₂, which was then graphitized, and ¹³C was determined by means of accelerator mass spectrometry (AMS) at the Australian National University, Canberra, Australia. The ¹³C concentration is given as percent modern carbon (pmc) and converted into the conventional radiocarbon age, with analytical errors of <0.22% and <55 a, respectively.

4. Results and discussion

4.1. Groundwater geochemistry evolution along the flow path

The principal characteristics of the surface water and groundwater and changes along the transect from the southwestern part of the basin (near Nanhu) to the northeastern part of the basin (near Xihu) are shown in Table 1 and Fig. 4. This transect represents the overall groundwater flow pattern within the Dunhuang Basin, and in Fig. 3, all of the groundwater sample locations are projected onto the corresponding position on this line. In the analysis, we divided the groundwater data into three groups based on the distance along the transect and the aquifer condition: the Nanhu group, the Dunhuang unconfined water, and the Dunhuang confined water. The samples from the Nanhu group are located around 10 km along the transect. The samples from Dunhuang group located between 20 km and 80 km along the distance to Danghe reservoir. The samples from Dunhuang unconfined aquifer include G5–G11, and the samples of G14–G19 belong to the Dunhuang confined aquifer. These groups are representative of the overall range of groundwater regimes in the Dunhuang oasis. In the Dunhuang Basin, the Danghe river flows along a channel approximately 60 km long, being the only perennial runoff flow into the oasis. The surface water for the Dunhuang oasis comes primarily from the Danghe reservoir. Despite the high evaporation in this region, the salinity of the surface water remains close to 340 mg L⁻¹ from the upstream reaches of the river to the downstream reaches, with the water chemistry belonging to the HCO₃⁻–Ca²⁺ type for most of the distance, but changing to HCO₃⁻–Na⁺ type at the last of the sample sites (samples S1–S3; Table 1).

The TDS of the groundwater increased along the flow direction in the study area. It was generally low in the Nanhu Irrigation District, with a mean concentration of 485 mg L⁻¹ and a range from 384 to 665 mg L⁻¹. In such arid regions, groundwater with TDS below 1000 mg L⁻¹ is thought to have good quality (He et al., 2012). The pH of the Nanhu water ranged between 7.70 and 8.30 (Table 1), indicating an alkaline nature. In the Dunhuang oasis, the salinity of the groundwater gradually increased along the transect. The TDS increased from 358 mg L⁻¹ to 2260 mg L⁻¹ in the unconfined groundwater and ranged between 724 mg L⁻¹ and 1729 mg L⁻¹ in the confined group, with no obvious trend along the transect (Table 1). The pH ranged from 6.82 to 8.56.

Generally speaking, the salinities of the groundwater were low in the Nanhu group and in the southern Dunhuang Basin, while higher salinity values were found in the north part of the Dunhuang Basin. This may be attributed to the different recharge mechanisms, and hydrogeochemical evolution as well as the effects of evaporation. In the Nanhu Basin, agriculture mainly relies on a spring-fed irrigation system. Many springs were found in this small basin, which provides an estimated 99 million m³ a⁻¹ of spring runoff. In the southern Dunhuang Basin, ancient riverbeds, which were formed by highly permeable cobbles, gravels, and sands, are widely distributed. As a result, the quality of the groundwater is generally good owing to significant recharge from surface water. However, in the northern part of the Dunhuang Basin, the groundwater table becomes shallow and the horizontal groundwater flow becomes very slow (Jia, 2006). In the arid environment, groundwater is lost by intensive evaporation and its salinity increases.

The major ions also showed a different trend along the flow path. In the Nanhu group, the ion concentrations were generally low (Fig. 4b–h). The Cl⁻, SO₄²⁻, and HCO₃⁻ concentrations averaged 79.7, 148, and 229 mg L⁻¹, respectively, in the Nanhu group. The cations in all of the groundwater samples were dominated by Na⁺, and for the anions, samples from a shallow well and a spring (G2 and G4, respectively) belonged to the SO₄²⁻ type, whereas the two deep samples (G1 and G3) belonged to the HCO₃⁻ type (Table 1).

In the Dunhuang oasis, the trends for the major ions differed between the unconfined and confined groups. A principal feature of the unconfined groundwater was enrichment of all ions except NO₃⁻ along the groundwater flow path. The Cl⁻, SO₄²⁻, Na⁺, and Ca²⁺ concentrations were below 150, 300, 150, and 100 mg L⁻¹, respectively, to a distance of 40 km from the start of the transect (Fig. 4b, c, e, and h). However, the ion concentrations increased sharply after a distance of 40 km from the start of the transect. It was especially noticeable for Cl⁻, SO₄²⁻, and Na⁺, which increased to 638, 868, and 727 mg L⁻¹ (G19), respectively (Fig. 4b, c, and e). The groundwater type changed from a HCO₃⁻-dominated type in the south, near the Mingsha Mountains to SO₄²⁻ type farther north, near the Danghe River (Table 1).

However, in the confined groundwater, the ions followed a sequence of geochemical evolution. The concentrations of SO₄²⁻ and Na⁺ are around 400 and 200 mg L⁻¹ in the middle of the transect, at about 40 km, but increase rapidly to 1100 and 504 mg L⁻¹ in well 17, which is located about 60 km from the start of the transect (Fig. 4c and e). The Cl⁻, Mg²⁺, and Ca²⁺ values in water from the confined aquifer generally remained stable or increased slightly along the transect (Fig. 4b, g, and h), and all of the groundwater in this group is SO₄²⁻ type.

The NO₃⁻ content shows irregular variation along the groundwater flow path (Fig. 4d). Most samples in the confined group had a relatively low NO₃⁻ content with values of 0–11.3 mg L⁻¹ (except for a value of 26.0 mg L⁻¹ in G14). The relatively low and steady concentration in the confined waters indicates that net NO₃⁻ loss is occurring and that anthropogenic inputs to this groundwater are negligible. In contrast, the unconfined groundwater had higher NO₃⁻ levels and high variation among the wells (Fig. 4d).
Table 1
Basic physical and chemical data for the groundwater and surface water samples obtained in the Dunhuang Basin.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Well depth (m)</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>TDS (mg L⁻¹)</th>
<th>Cl⁻ (mg L⁻¹)</th>
<th>NO₃⁻ (mg L⁻¹)</th>
<th>SO₄²⁻ (mg L⁻¹)</th>
<th>HCO₃⁻ (mg L⁻¹)</th>
<th>Na⁺ (mg L⁻¹)</th>
<th>K⁺ (mg L⁻¹)</th>
<th>Mg²⁺ (mg L⁻¹)</th>
<th>Ca²⁺ (mg L⁻¹)</th>
<th>δ¹⁸O (%)</th>
<th>δ³⁴S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>18.4</td>
<td>8.30</td>
<td>384</td>
<td>57.8</td>
<td>3.11</td>
<td>101</td>
<td>200</td>
<td>72.6</td>
<td>3.78</td>
<td>13.4</td>
<td>40.2</td>
<td>-10.5</td>
<td>-75.8</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>15.8</td>
<td>7.96</td>
<td>438</td>
<td>80.4</td>
<td>3.80</td>
<td>148</td>
<td>162</td>
<td>85.8</td>
<td>4.70</td>
<td>15.1</td>
<td>44.8</td>
<td>-10.5</td>
<td>-75.4</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>16.8</td>
<td>7.70</td>
<td>665</td>
<td>100</td>
<td>0.00</td>
<td>186</td>
<td>371</td>
<td>115</td>
<td>6.75</td>
<td>23.1</td>
<td>95.7</td>
<td>-10.9</td>
<td>-73.6</td>
</tr>
<tr>
<td>4</td>
<td>Spring</td>
<td>16.8</td>
<td>7.80</td>
<td>452</td>
<td>79.7</td>
<td>3.75</td>
<td>157</td>
<td>181</td>
<td>93.0</td>
<td>4.68</td>
<td>14.5</td>
<td>49.4</td>
<td>-10.9</td>
<td>-77.6</td>
</tr>
</tbody>
</table>

The K⁺ content in the unconfined water increased steadily from 3.63 mg L⁻¹ at the start of the transect to 12.3 mg L⁻¹ at the end of the transect. In the confined group, the K⁺ content generally remained stable, with values of 5.8–10.9 mg L⁻¹. Confined aquifer systems have been used as water resources in many regions around the world because their compositions are stable and because the water is not easily polluted. In general, the confined groundwater in the Dunhuang Basin has higher K⁺ and lower NO₃⁻ contents than the unconfined water, which suggests that internal sources of salinity may contribute greatly to the water’s chemical evolution along the transect.

The chemical species dissolved in groundwater are not independent, and the relationships between various ions can be used to study the characteristics and mineralization sources of the groundwater (Schoeller, 1977). In particular, the Cl⁻ ion undergoes few chemical and biological reactions in a natural environment and has, therefore, been widely used as a conservative reference element to study water–rock interactions (Edmunds et al., 2002; Zhu et al., 2008). In arid regions, Cl⁻ mainly originates from the dissolution of halite in evaporite deposits, and its content increases when intense evaporation occurs along the flow path.

The linear relationships between Na⁺ and Cl⁻ and between K⁺ and Cl⁻ were strong and significant, with correlation coefficients (R²) of 0.86 and 0.64, respectively (Fig. 5a and b). This suggests that the dissolution of halite and sylvite strongly control the concentrations of these three ions. Groundwater was far below saturation with halite, as the calculated saturation index (SI) values were negative in all of the samples (Table 2), which confirms that halite minerals in the fine-grained sediments can easily enter the groundwater. According to the field survey carried out by the Gansu Geology Survey (1978), the soils of this area are rich in evaporite minerals such as halite, sylvite, gypsum and sodium sulfate (Glauber’s salt). The Na⁺/Ca²⁺ ratios vary between 0.5 and 4, and increase along the groundwater flow direction (Fig. 5c), indicating that in addition to the evaporation effect, hydrogeochemical processes are an important control on the groundwater chemistry. The mNa⁺/Cl⁻ ratio was investigated to shed further light on the origin of the Na⁺. These ratios are greater than 1 in all of the ground-water samples except sample 8 (Fig. 5a), indicating that there is much more Na⁺ than Cl⁻. One possible source for this excess is the weathering of feldspar via a reaction such as the following:

\[ 2NaAlSiO₄ + 9H₂O + 2H₂CO₃ = Al₂Si₃O₈(OH)₄ + 2Na⁺ + 2HCO₃⁻ + 4H₄SiO₄⁻ \]

This reaction could produce kaolinite as a subsequent mineral, and fieldwork indicated widespread occurrence of kaolinite in weathered rocks in the study area. This also can be confirmed by the relationship between Na⁺/Cl⁻ (K⁺/Cl⁻) and Cl⁻ (or TDS), the values of Na⁺/Cl⁻ (K⁺/Cl⁻) were relatively high in the less saline groundwater (Fig. 5a, b, and d), and the maximum value reached 3 for Na⁺/Cl⁻, showing a decrease with increasing Cl⁻. Sodium sulfate is another potential source of Na⁺ and the Na⁺ and SO₄²⁻ concentrations were strongly and significantly correlated (R² = 0.82; Fig. 5e), suggesting that weathering of Glauber’s salt is common in the groundwater of the study area. Indeed, Glauber’s salt is an important mineral product that is mined near Dunhuang City. Calcium and SO₄²⁻ showed some correlation with one another, the R² was 0.42, suggesting that simple gypsum dissolution may exert some control on the Ca²⁺ chemistry. However, there is too little Ca²⁺ relative to SO₄²⁻ for gypsum alone to be responsible for SO₄²⁻ chemistry (Fig. 5f). This must be supplied by the dissolution of Glauber’s salt.

In the plot of Mg²⁺ + Ca²⁺ as a function of SO₄²⁻ + HCO₃⁻, the data did not follow a 1:1 stoichiometry ratio (Fig. 5g), indicating that SO₄²⁻, HCO₃⁻, Mg²⁺, and Ca²⁺ were not derived from the simple dissolution of calcite, dolomite, and gypsum. The total Mg²⁺ + Ca²⁺ was deficient relative to the total SO₄²⁻ + HCO₃⁻, and this deficiency must be balanced by excess Na⁺ produced from the Glauber’s salt and feldspar discussed earlier in this section. The SI values for calcite and dolomite were both positive in all samples except well 5 (Table 2), showing that the dissolution of these two minerals in groundwater must be weak. The Mg/Ca ratio of the dolomite and limestone in the aquifers is a dominant factor that determines...
the $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratio of the groundwater; this is because of incongruent dissolution. However, this trend is controlled by the solubility equilibrium as well as the contact surface between water and rocks. Thus, the $\text{Mg}^{2+}/\text{Ca}^{2+}$ of groundwater will not be very high, although it is likely to be higher than the ratio in minerals. The mean $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the Dunhuang groundwater was 0.66, which indicates that the reaction between water and dolomite, for which $\text{Mg}^{2+}/\text{Ca}^{2+} = 1$, is relatively minor. Therefore, the dissolution of carbonate minerals and carbonate cements yields $\text{Ca}^{2+}$ to the groundwater, thereby exerting a strong influence on groundwater salinity. As a result, the low concentration of $\text{Mg}^{2+}$ in the groundwater mainly resulted from a lack of $\text{Mg}^{2+}$. In addition, the high saturated index of the samples with respect to dolomite (Table 2) indicated removal of $\text{Mg}^{2+}$ from the groundwater.

The evolution of salinity in the groundwater was also explored using a plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ versus $(\text{Na}^+ + \text{K}^+)$ (Fig. 5i). The array of data points passed through a line with a slope of $-0.88$ ($R^2 = 0.90$), indicating that essentially all of the $\text{Na}^+$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ participated in ion-exchange reactions. In unconsolidated sediments of an aquifer system, there is always a considerable amount of clay minerals that adsorb some of the cations in their pore space. This allows some species of cations in the groundwater to be replaced by other cations from the aquifer. To provide more insights into the ion-exchange and reverse ion-exchange reactions that affect the groundwater chemistry, Schoeller (1965) defined two chloroalkaline indices:

\[ \text{CAI}_1 = \text{Cl}^- - \frac{[(\text{Na}^+ + \text{K}^+)/\text{Cl}^-]}{2} \]

\[ \text{CAI}_2 = \text{Cl}^- - \frac{[(\text{Na}^+ + \text{K}^+)/\text{SO}_4^{2-}]}{2} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^- \]

Fig. 4. Changes in the properties of groundwater along the transect from the southwestern part of the Dunhuang Basin (near Nanhu) to the northeastern part (near Xihu). (a) TDS, (b) $\text{Cl}^-$, (c) $\text{SO}_4^{2-}$, (d) $\text{NO}_3^-$, (e) $\text{Na}^+$, (f) $\text{K}^+$, (g) $\text{Mg}^{2+}$, and (h) $\text{Ca}^{2+}$. 
J. Ma et al. / Applied Geochemistry 28 (2013) 19–31
When there is an exchange occurs between Na⁺ in the groundwater and Ca²⁺ or Mg²⁺ in the aquifer materials, both of the indices are positive, indicating ion exchange of Na⁺ in groundwater with Ca²⁺ or Mg²⁺ in the alluvium or weathered materials. Fig. 5j shows that both calculated indices were positive (above 0) in most of the samples, indicating that reverse ionic exchange took place and increased the hardness of these waters.

4.2. Groundwater recharge based on stable isotope ratios

The stable isotope ratios ($\delta^2$H and $\delta^{18}$O) can provide information on the mode of recharge of the water and can further explain groundwater origins. Fig. 6 shows the stable isotope data for all surface water and groundwater samples in the study area and related data for possible recharge sources within the two meteoric...
In a previous study (Ma et al., 2009), the authors determined the LMWL for meteoric water line [LMWL] for northwestern China). In a previous study, the three groups of samples were distinct. In the Nanhu Irrigation District, the unconfined groundwater has a narrow range, with values between −10.9% and −10.5% for δ18O and between −77.6% and −73.6% for d2H. The mean δ18O and d2H values in the Dunhuang unconfined groundwater tended to become increasingly enriched along the groundwater flow path from SW to NE, increasing from −11.0% to −7.5% for δ18O and from −76.3% to −61.5% for d2H, with averages of −9.7% and −71.9%, respectively. In contrast, groundwater extracted from confined aquifers was relatively depleted in heavy isotopes, with mean values of −10.4% δ18O and −74.4% d2H.

Six possible recharge categories may act on the aquifers of the Dunhuang Basin: modern and past local rainfall, modern and past local irrigation, modern and past local drainage, modern and past interbasin drainage, modern and past interbasin drainage channels, and modern and past interbasin drainage channels in the Sanwei Mountains. The precipitation has a relatively high isotope value and is strongly influenced by evapotranspiration processes in the arid northwestern region of China and appears to provide a good representation of conditions in this region (Ma et al., 2009, 2010).

The groundwater of the Dunhuang Basin had δ18O values ranging from −7.5% to −11.3% and δ2H values ranging from −61.5% to −84.3% (Table 1), with corresponding average values of −10.1% and −73.4%. However, the isotopic compositions of the three groups of samples were distinct. In the Nanhu Irrigation District, the δ18O and δ2H values of groundwater had a narrow range, with values between −10.9% and −10.5% for δ18O and between −77.6% and −73.6% for δ2H. The mean δ18O and d2H values in the Dunhuang unconfined groundwater tended to become increasingly enriched along the groundwater flow path from SW to NE, increasing from −11.0% to −7.5% for δ18O and from −76.3% to −61.5% for d2H, with averages of −9.7% and −71.9%, respectively. In contrast, groundwater extracted from confined aquifers was relatively depleted in heavy isotopes, with mean values of −10.4% δ18O and −74.4% d2H.

Six possible recharge categories may act on the aquifers of the Dunhuang Basin: modern and past local rainfall, modern and past river infiltration, irrigation returns, and lateral groundwater flow. Modern local rainfall recharge is affected by the O and H isotopic compositions of the precipitation. This region is strongly influenced by westerly air masses throughout most of the year (Tian et al., 2007). The precipitation has a relatively high isotope value of around −4% δ18O in the summer and a low of −16% δ18O in winter, which agrees with observations from other areas of northwestern China that are controlled by a similar climate system (Tian et al., 2007; Wu et al., 2011; Zhao et al., 2011). Furthermore, most of the rainfall occurs during the summer months; based on data from local weather stations from 1938 to 1980, it accounted for 78.5% of the overall precipitation. Therefore, modern rainfall recharge is dominated by summer precipitation. Since there are no long-term data on isotope ratios in the Dunhuang Basin, data from the Zhangye Meteorological Station, which is located some 580 km SE of Dunhuang City and has been one of the members of the IAEA network since 1985, was chosen. The weighted mean values of δ18O and δ2H at Zhangye were −6.3% and −43.2%, respectively (IAEA and WMO, 2004). Compared with these values, all of the groundwater samples were strongly depleted, indicating that there has been no modern direct recharge of the groundwater aquifers by rainfall in the plains area. In addition, the average direct recharge rate calculated based on Cl− mass-balance calculations is 0.95–3.0 mm a−1 in nearby regions with an annual rainfall of 89–120 mm a−1 in the Minqin Basin and the Badain Jaran Desert (Edmonds et al., 2006; Ma and Edmunds, 2006). This also suggests that precipitation in the plains area had a negligible impact on the groundwater. Many arid regions, such as Australia and southwestern USA, have experienced little or no direct recharge (≤0.01 mm a−1) for millennia (Allison et al., 1990; Scanlon et al., 2004).

Modern surface runoff recharge mainly consists of water from the Danghe River and some small, intermittent rivers from Sanwei mountain that flow only after rainfall events. The isotope values from the up stream of the Danghe river were −11.1% δ18O and −76.4% d2H. These values are similar to those reported from the Dunde ice core in the the Qinghai–Tibetan Plateau (Thompson et al., 1989), suggesting that the meltwater from the southern Qilian Mountains may contribute to the composition of the river water, and thus contribute significantly to the steady long-term runoff of this river. The isotope ratios of water collected from drainage channels in the Sanwei Mountains were −11.7% for δ18O and −84.3% for d2H. The isotopic characteristics of the Nanhu groundwater is similar to the surface water of Danghe River (Fig. 6), indicating that the groundwater may originate from surface runoff of Danghe River. Every year, approximately 99 million m3 of water is discharged from the Danghe River into the Nanshan district (Jia, 2006). In addition, some intermittent rivers such as the Cuimutu and Shanshui valleys that originate from summer floods may also contribute to recharge, although this is very limited. The water quickly enters the aquifers in the mountain-front piedmont and then overflows as springs. The water resource is relatively steady because of this stable recharge.

There is some variation in the stable isotope composition among sites in the Dunhuang unconfined groundwater, indicating a degree of heterogeneity in the modern aquifer. Samples G5, G6, and G7, which are located near the banks of the Danghe River in the southern Dunhuang Basin, and G8, located at the outlet of the Dongsu River, had low values (δ18O < −10.0% and d2H < −73.0%), these being close to those of the groundwater in Nanhu group, indicating the presence of rapid recharge due to the rapid movement of the river at the mountain-front. The sample from the famous Moon Spring (G13) had the heaviest isotope values, −7.5% δ18O and −61.5% d2H, revealing the occurrence of strong evaporation when the groundwater emerges. The total annual runoff from the Xishui and Dongsu rivers is nearly 5.6 × 106 m3 a−1, and all of the water infiltrates into the aquifer along the 2.5-km course of the rivers. In addition, the 43 × 106 m3 a−1 runoff from the Danghe River leaks into the subsurface over a distance of 20 km from the river outlet. This must provide a significant modern recharge to the Dunhuang oasis. In the northern part of the basin, the unconfined groundwater has higher isotopic values (G9, G10, G11) that lie well below the LMWL, reflecting an influence of evaporation and possible mixing with irrigation water. The isotopic composition of some of the confined water also indicates considerable modern recharge.

Lateral groundwater flow that recharge the aquifer can also be defined by isotopic signatures, since these flows have different origins and different evolutionary processes. At the southern margin of the basin, there is also an influx of water from the Shanshui Valley, which has a relatively high δ18O value (−6.3% or −43.2%) and a low d2H value (−84.3%), indicating that this water is sourced from the Qilian Mountains. This water may contribute to the lateral recharge of the aquifers in the southern part of the basin.
of the basin, the groundwater flows are likely to be blocked by large faults (Fig. 2). In the eastern region, the isotopic signatures of the two samples from the nearby Guazhou aquifer were markedly different (1.47‰ δ18O heavier) from that in the Dunhuang Basin (Fig. 6), indicating that the lateral groundwater flow from the Guazhou system to Dunhuang Basin is very limited. The amount of lateral groundwater flow from Guazhou to Dunhuang is only 20,000 m³ a⁻¹ (Jia, 2006). Currently, rapid urbanization and the expansion of agriculture near Guazhou have placed great pressure on the region’s natural water resources, and thousands of wells have been drilled in oasis areas, leading to excessive withdrawal of groundwater and a rapid fall in groundwater level, which has lead to reduced lateral groundwater flow from Guazhou to Dunhuang.

In arid regions, ancient water circulates in the deepest confined parts of an aquifer. This can be distinguished from modern water based on differences in the isotopic ratios, since these are depleted in ancient water compared with modern water and are, therefore, shifted in their position along the GMWL towards more negative values (Celle-Jeanton et al., 2009; Ma et al., 2010). The deep confined water in the northern Dunhuang Basin is greatly depleted, with extreme values of −11.3‰ for δ18O and −84.3‰ for δ2H (G17), both of which lie below the LMWL, showing the occurrence of evaporation from an isotopically depleted source. Compared to the modern local rainfall and runoff from the Danghe Reservoir, the groundwater is significantly depleted, suggesting that recharge occurred under a cooler climate in the past. According to the temperature−δ18O relationship in local rainfall, the calculated recharge temperature would be about 6.7 °C, which is in line with previous observations from the Heihe River Basin and the Shiyanqhe River Basin in northwestern China (Edmunds et al., 2006; Zhu et al., 2008). Many studies conducted in the Hexi corridor have found palaeowaters that originated in the late Pleistocene from nearly 40 ka BP (Ma et al., 2005; Su et al., 2009; Yang et al., 2011).

4.3. Residence time based on 14C data

Radiocarbon activity in the inorganic C (as HCO₃⁻) in groundwater has been widely used to establish groundwater residence times, since 14C, which originated from the atmosphere during the initial recharge, would decay with a half-life of approximately 5.73 ka (Godwin, 1962). However, the groundwater undergoes many reactions during recharge and flow processes, such as congruent and incongruent reactions with carbonate minerals, mixing with older or more recent water, as well as continuous exchange with the atmosphere under closed system conditions. All of these processes would affect the 14C activity associated with the total dissolved inorganic C in the groundwater. Hence, it is very difficult to determine absolute ages. Many models have been used to correct radiocarbon data (Tamers and Thielen, 1966; Mook and Koene, 1975; Pearson et al., 1978; Fontes and Garnier, 1979; Eichinger, 1983; Gonfiantini, 1988). But here the radiocarbon data are used only semi-quantitatively. In northwestern China, an upper limit of about 80 pmc for initial 14C activity has been broadly used (Edmunds et al., 2006; Zhu et al., 2008; Ma et al., 2010), which is quite similar to the value used in the study by Vogel (1970) in Western Europe and South Africa. Table 3 summarizes the results of the radiocarbon analyses in the present study. The groundwater exhibited radiocarbon activities ranging from 13.9 to 79.6 pmc. The unconfined waters had 64.9−79.6 pmc, and are, therefore, relatively young. In contrast, the confined water had uncorrected ages ranging from 3.30 ka (G14) to more than 15 ka (G17). It was found that the confined groundwater near the piedmont in the southern part of the Dunhuang Basin had a value of 65.9 pmc (G14), which was younger than the water from the discharge zones, indicating rapid recharge within the saturated zone through river channels mixed with palaeowater at greater depths in the aquifer. At the northern edge of the basin, the confined groundwater, (13.9 pmc and an uncorrected age of ~15 ka (G17) indicated a much older water. The stable isotopes in this water were also the most depleted (−11.26‰ δ18O and −84.34‰ δ2H), supporting the indicative age and also suggesting that recharge occurred during a colder humid period of the late Pleistocene.

![Fig. 6. Plot of the relationship between δ18O and δ2H for groundwater, surface water, and possible recharge sources in the study area. LMWL, local meteoric water line for northwestern China; WMWL, world meteoric water line.](image-url)
4.4. Conceptual model for groundwater recharge

A conceptual model for groundwater recharge is proposed based on the isotopic data (Fig. 7). The rainfall was more abundant in the region during the late Pleistocene and the aquifer was probably replenished by rainfall through mountain-front recharge and direct diffusive recharge. However, modern direct infiltration provides negligible recharge to the shallow unconfined aquifer. Most recharge originates from the Qilian and Sanwei Mountains where there is higher precipitation and melt water. The natural rivers in the oasis area have mostly been changed to artificial channels, the seepage from which plus irrigation return water are the main recharge sources for the shallow phreatic aquifer. The confined aquifer of the piedmont has been recharged through a number of mechanisms, including lateral flow from the piedmont and modern water through directly vertical infiltration from river channels. Groundwater in the confined aquifer flows towards the discharge zones to the NE.

The groundwater flow velocity can be estimated using the difference in dates and positions between the two confined groundwater samples: sample G17 (~15 ka) is about 31 km further along the flow path from sample G14 (~3.3 ka), indicating an approximate flow velocity of 2.65 m a⁻¹. This result is coincident with that calculated based on Darcy’s law. The average flow velocity of the deep groundwater is 2.92 m a⁻¹, assuming a porosity of 0.26, saturated hydraulic conductivity of 6.45 m day⁻¹, and a hydraulic gradient of 3.2 × 10⁻⁴ (Masch and Denny, 1966). This indicated that groundwater flow is relatively slow and that the water resources sustained by this flow are essentially non-renewable in the confined aquifer. In summary, the confined groundwater dates back to the late Pleistocene and has continued throughout the Holocene, as discussed in other basins in northwestern China (Chen et al., 2006; Ma et al., 2010). The aquifer system retains this ancient groundwater, but also reveals modern recharge (particularly in unconfined aquifers) as well as mixing of water from different periods.

5. Conclusions

Isotopic data and hydrogeochemical tracers were used to understand the recharge and geochemical evolution of groundwater in the Quaternary aquifers beneath the Dunhuang Basin. The Quaternary aquifers are all closely connected with streams originating in the Qilian Mountains. The mean values of δ¹⁸O and δ²H in the unconfined groundwater tended to be enriched along the overall groundwater flow path from the SW to the NE, increasing from −11.0‰ to −7.5‰ for δ¹⁸O and from −76.3‰ to −61.5‰ for δ²H, respectively. In contrast, groundwater from confined aquifers was depleted in heavy isotopes, with a mean δ¹⁸O of −10.4‰ and δ²H of −74.4‰. The values in surface runoff and meltwater from the Qinghai–Tibetan Plateau south of the study area suggest that meltwater from the Qilian Mountains strongly determines the isotopic composition of water in the Danghe River, and contributes significantly to the steady long-term runoff of this river. However, the stable isotope data, which are markedly depleted in heavy isotopes compared to modern rainfall in the plains area, clearly indicate that there is no direct relationship between the confined groundwater and modern direct recharge. The groundwater exhibited a range of radiocarbon activities from 13.9 to 79.6 pmc, with younger water in the upper reaches of the Danghe River and older water in the lower reaches. The unconfined water was generally young with 64.9–79.6 pmc. At the northern edge of the basin, confined groundwater was much older, with a radiocarbon content of 13.9 pmc, indicating an age of ~15 ka, which corresponds to the humid climatic phases of the late Pleistocene.

The strong and significant linear relationships between Na⁺ and Cl⁻ and between K⁺ and Cl⁻ indicate that the dissolution of halite and sylvite strongly control the concentrations of these three ions. Groundwater was far below saturation for halite, so halite minerals in the fine-grained sediments can easily enter the groundwater. The Na⁺/Cl⁻ molar ratio values were all >1 in the groundwater, indicating the presence of excess Na⁺, possibly due to the weathering.

Fig. 7. Conceptual diagram of recharge to the Quaternary aquifer beneath the Dunhuang Basin.
of feldspar. Sulfate, HCO\textsubscript{3}, Mg\textsuperscript{2+}, and Ca\textsuperscript{2+} were not derived from the simple dissolution of calcite, dolomite and gypsum.

The results have important implications for management of the inter-basin water allocation programme and groundwater resources in the Dunhuang Basin, one of several water-stressed basins in northwestern China that lies in a region designated for rapid development under China’s West Development Strategy. Since most of the deep groundwater resources derived from recharge during a period with a colder and wetter climate, exploitation of this groundwater is considered to be “mining” if it cannot be replenished. The glaciers of the Qilian Mountains have exhibited large absolute losses and the altitude of the equilibrium line has generally increased because the ablation rate has exceeded the mass accumulation rate as a result of global warming since 1950 (Ding et al., 2006; Wang et al., 2010, 2011). This has significantly influenced the sustainable source of Danqiu River and recharge of the unconfined groundwater. However, the groundwater has seen over-exploitation due to a lack of knowledge of recharge and evolution mechanism. The results of this study will help the local government to protect this limited and precious water resource. A rational land-use plan for agriculture, forestry and animal husbandry to regulate water allocation on a whole-basin basis should be set up.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 41271039), the Fundamental Research Funds for the Central Universities, and the Keygrant Project of the Chinese Ministry of Education (No. 310005). This work also forms part of the 111 project (No. B06026) and the wider UK–China collaboration which greatly improved the paper.

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