Groundwater Recharge and Mixing in Arid and Semiarid Regions: 
Heihe River Basin, Northwest China

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Abstract: A sound understanding of groundwater recharged from various sources occurring at different time scales is crucial for water management in arid and semi-arid river basins. Groundwater recharge sources and their geochemical evolution are investigated for the Heihe River Basin (HRB) in northwest China on the basis of a comprehensive compilation of geochemical and isotopic data. Geochemical mass-balance modeling indicates that mountain-block recharge accounts for a small fraction (generally less than 5%) of the shallow and deep groundwater sustaining the oasis, whereas infiltration of rivers and irrigation water contribute most of the groundwater recharge. Dedolomitization is the primary process responsible for the changes in groundwater chemical and carbon isotope compositions from the piedmont to the groundwater discharge zone, where the dedolomitization is very likely enhanced by modern agricultural activities affecting the shallow groundwater quality. Analysis of radioactive isotopes suggests that these primary recharge sources occur at two different time scales. Radiocarbon-derived groundwater age profiles indicate a recharge rate of approximately 12 mm/year, which probably occurred during 2000–7000 years B.P., corresponding to the mid-Holocene humid period. The recharge of young groundwater on the tritium-dated time scale is much higher, about 360 mm/year in the oasis region. Infiltration from irrigation canals and irrigation return flow are the primary contributors to the increased young groundwater recharge. This study suggests that groundwater chemistry in the HRB has been influenced by the complex interaction between natural and human-induced geochemical processes and that anthropogenic effects have played a more significant role in terms of both groundwater quantity and quality.

Key words: Heihe River Basin, groundwater recharge, groundwater mixing, isotope hydrology

1 Introduction

The Heihe River Basin (HRB) is one of a series of inland river basins directly fed by rivers originating in the Tibetan Plateau (Fig. 1). The middle reach of the river, located in the central part of a long, narrow stretch of alluvial deposits forming flat land referred to as the Hexi Corridor, has been a critical region for socio-economic development for the past 2,000 years as part of the ancient Silk Road (Li, 1995). The HRB, which is a typical region in arid and semiarid northwestern China, has been the focus of attention because of its increasing water stress and environmental degradation (Chen et al., 2014). The HRB is highly reliant on the Heihe River for water supplies; consumption of water resources by humans has resulted in the reduction of river runoff and spring flow (Chen, 1990). The Zhangye Basin is the largest oasis in the HRB and consumes ~86% of diverted water for irrigation (Chen, 1990). The conflict between grain production to feed the increasing population and the water demand of the ecosystem has become a topic of great interest to researchers and policy makers. As a result of a government mandate to release a guaranteed amount of river water to downstream areas, groundwater has become a more important water supply source in the HRB (Cheng

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et al., 2014; Yao et al., 2015; Wu et al., 2015). Understanding of groundwater recharge sources for those alluvial aquifers, geochemical evolution of groundwater, and mixing of groundwater of different residence times will enable a more sustainable development of groundwater resources.

The natural hydrological cycle has been strongly affected by human activities, such as construction of reservoirs and irrigation canals and replacement of spring flow irrigation by well irrigation. Groundwater overexploitation is an obvious reason for water-level decline and degradation of the hydrogeological regime (Gates et al., 2008). Most studies that have been conducted since the early 1980s have focused on water-balance evaluation based on the monitoring of groundwater level and groundwater chemical property variations from collecting geochemical data at multiple scales in time and space (e.g., Zhang, 2005). Monitored groundwater level dynamics can reflect variations of hydraulic factors, but only at decadal timescales, and geochemical indicators are possibly affected by chemical materials used in agricultural activities. Although environmental tracers have been used in recent geochemical investigations to estimate groundwater residence time and groundwater recharge (e.g., Chen et al., 2006; Chen et al., 2007; Gates et al., 2008; Chen and Wang, 2009; Chen et al., 2014; Gong et al., 2014), comprehensive studies synthesizing these data to establish a solid understanding of the groundwater system are rarely conducted.

The objectives of this study are to synthesize a large amount of geochemical and environmental tracer data acquired during the past 10 years to provide a comprehensive understanding of the groundwater evolution in the HRB. Groundwater sources, recharge history, and timing in relation to climatic fluctuations and anthropogenic effects, and mixing of groundwater with different residence times are evaluated using geochemical mass-balance modeling and a conceptual groundwater mixing model. The geological controls on groundwater quality and environmental tracer indicator concentrations and subsequent impacts of agricultural development in the past several decades are also considered. This paper also presents the original finding that the dedolomitization process that affects the groundwater geochemical evolution in the oases is mostly related to fertilizer application in the irrigated agricultural fields.

2 Geological Settings

The Heihe River catchment covers an area of approximately 130,000 km², and the HRB is divided into four management groundwater basins: the Zhangye Basin (ZYB) and the Jiuquan Basin (JQB) are located in the middle reach, and the Jinta Basin and Ejina Basin (EJB) are located in the lower reach (Fig. 1). The Heihe River originates in the mountains, flows through these basins, and finally discharges into inland lakes or dissipates in the deserts in the EJB (Fig. 1). The landscape in this region is controlled by water availability: in the piedmont region, where the groundwater table is deep and regions where surface water is scarce, the landscape is typical of the Gobi Desert; in central parts of the valley, where the groundwater table becomes shallower and a dense canal system has been developed to divert river water for irrigation, the landscape is dominated by natural and artificial oases. These basins originated from Cenozoic or Mesozoic–Cenozoic basins controlled by neotectonics, especially the strong upthrust in front of the mountain range (Chen, 1994). All primary aquifers are formed of Quaternary sediments comprising thick unconsolidated gravel and sand in the piedmont region and becoming thinner and finer sand deposits interbedded with clay layers in the central valley. The aquifer systems consist of deposits of the Yumen Formation (Q₁) and the Jiuquan Formation (Q₂), which have a total thickness of 500–1,000 m. Detailed descriptions of this area can be found in many previous studies (e.g., Fan, 1983; Chen, 1990; Zhang, 2005).

Investigation of groundwater flow in the HRB began in the 1950s. A highly controversial issue is the hydrologic properties of the active Qilian Mountains–Hei Corridor faults system, which is a series of reverse faults along the mountain front (Li et al., 1999). The reverse faults are generally classified as low-permeability structures and the great fault zone is inferred to act as a hydraulic barrier to lateral groundwater flow (e.g., Fan, 1962; 1983). This proposition has been widely accepted when evaluating groundwater balance and flow patterns; the primary recharge sources are mountain-front recharge (MFR) occurring as river leakage in the transition zones between the mountains and the central valley and through the underflow along the river valley (e.g., Zhang, 2005; Ding et al., 2012). Contrast views on the hydraulic properties of the great fault zone are mainly based on analogies with other intermountain basins where there may be considerable lateral groundwater (e.g., Duan, 1964) or simple end-member geochemical mixing analysis of groundwater salinity (Yao et al., 2001). Chen et al. (2014) suggested that groundwater in the ZYB can receive glacier meltwater sourced in the mountains through deep faults, primarily on the basis of stable isotope anomalies in groundwater. However, the stable isotopes should not be capable of distinguishing mountain-block recharge (MBR) from river leakage because both the sources could carry a
depleted, high-elevation signal (Manning and Solomon, 2004). Additionally, the stable isotope composition of water may also be affected by local evaporation, further biasing the derived source interpretations.

The distribution of MFR has been modified by human activities in the past decades. River leakage is generally greater in the upstream part than in the downstream region of the MFR zone (Covino and McGlynn, 2007). However, approximately 80% of runoff exiting the mountains has been diverted through cement/stone-lined canals from the Yingluo Gorge reservoir to the downstream Longshou Hydropower Station and the Caotanzhuang Water Division Project (Hu et al., 2012). Gauge runoff measurements conducted from May to October 2010 (a typical high-water-stage period) indicated that the total river leakage between Caotanzhuang (9.0 km downstream of the Yingluo Gorge reservoir) and a gauge installed at the downstream end of the MFR zone accounted for ~70% of the runoff (Hu et al., 2012). Because of the sloping ground surface northwestward from the mountain front, the alluvial fan to the west of the Heihe River is the primary MFR zone, while the east receives leakage of diverted water for irrigation. The great thickness of the gravel aquifer and the deeply buried groundwater level allow the aquifer system to serve as a great subsurface reservoir for groundwater storage.

Groundwater is mainly discharged from the aquifers as springs in the front of the alluvial fans and seepage to the
Heihe River along the valley bottom at a rate of ~50 m$^3$/s during 1967–2006 (Ding et al., 2009). Groundwater discharge has decreased since the early 1990s for several reasons (Ding et al., 2001): (1) increased groundwater withdrawal for irrigation and industry usage; (2) increased numbers of river water diversion canals that have been changed to cement lining; and (3) declines in local precipitation. Groundwater level fluctuations in representative wells reflect the same decreasing trend (Hu and Lu, 2009). After 2000, when the water diversion was reduced to increase the amount of runoff flowing to the downstream basins, groundwater pumping was increased and irrigation return flow became an important water balance term in the cultivated oases. In Gobi areas, where groundwater discharge channels to rivers are blocked by bedrock uplift, groundwater discharges mostly through evaporation at the shallow water table, accompanied by increasing groundwater and soil salinity (Li and Hao, 1999).

Geochemical and environmental tracer data have shown that groundwater in the shallow aquifers is derived from mixing of groundwater flow over different time scales. Tritium, CFC, and radiocarbon have been used to date groundwater (Chen et al., 2010; Qian et al., 2008; Qin et al., 2011; Yang et al., 2011). Groundwater radiocarbon ages of up to ~9000 years and high tritium concentrations in nearby aquifers of rivers suggest different time scales of recharge (Chen, 2006). Previous studies using CFC data have shown that most shallow groundwater in the irrigated area has mixed with young irrigation water, and the increasing irrigation since the 1980s has become a primary source of groundwater recharge (Qin et al., 2011). Chen et al. (2010) suggested that shallow groundwater may also receive upward leakage of deep groundwater with low solute concentration. Although the recharge from young irrigation water may control the current groundwater recharge in the irrigated area, estimation of natural groundwater recharge is also important for understanding the system and for water resources management.

3 Samples and Methods

3.1 Hydrogeochemical and Isotope Data

Previously reported surface water and groundwater analyses (Nie, 2004; Wen et al., 2008; Feng et al., 2004; Zhu et al., 2008; He et al., 2012; He et al., 2013) were systematically collected to provide coverage over the entire middle reach of the HRB (Fig. 2), including 8 for rivers, 7 for springs, 22 shallow (depth to well bottom from water table <100 m) wells in the oases, 16 oasis deep (depth to well bottom from water table >100 m) wells, and

![Fig. 2. Piper diagram of groundwater (226 samples) in the Zhangye and Jiuquan basins of the HRB. Data are combined from Nie (2004), Wen et al. (2008), Feng et al. (2004), Zhu et al. (2008), He et al. (2012), and He et al. (2013).](image-url)
26 wells in the Gobi area. All the collected wells can be located and have stable isotope data available: 17 of these wells are particularly monitored and have detailed well construction information available, and the remaining wells are pumped for irrigation or rural water supply. A total of 54 tritium measurements were collected, including 3 river samples obtained where rivers flow out of mountains, 7 springs, 22 shallow wells in the oases, 16 oasis deep wells, and 6 Gobi plain wells. A total of 35 radiocarbon data were collected: 1 spring, 10 oasis shallow wells, 9 oasis deep wells, and 15 Gobi plain wells. The geochemical evolution of all groundwater analyses for which both geochemical and radiocarbon information were available were evaluated. The mixing ratios of young and old groundwater were estimated on the basis of radiocarbon/tritium data pairs (28 pairs) using a binary mixing model of lump parameter models. Profiles of radiocarbon and tritium were used to estimate groundwater recharge at different time scales.

3.2 Geochemical mass-balance modeling

Groundwater geochemical mass-balance models among samples were constructed using the NETPATH code (Plummer et al., 1994). Because sample pairs along specific flow paths are generally difficult to identify, samples thought to be representative of source-water compositions were selected. Each groundwater sample composition was assumed to be the result of evolution from river water with alteration by mixing of groundwater inflow from mountain blocks, evaporation, and water–rock reactions. The average compositions of samples from the Yingluo Gorge and five rivers in the JQB were used to represent the chemical compositions of surface water in the ZYB and the JQB, respectively. Samples from mountain-front bedrock springs were used to represent the chemical composition of lateral groundwater inflow from mountains or the MBR. Phases considered in the geochemical models include calcite, dolomite, gypsum, and halite, as well as (Ca+Mg)/Na exchange and dissolution of CO₂.

3.3 Calculation of the groundwater mixing ratio

Groundwater is derived from young localized recharge mixing with old background groundwater. Although many mixing models are theoretically available, a simple binary mixing model can explain the tritium and radiocarbon data. The modeled tracer concentration in a sample is given as follows:

\[ C_{\text{cal}} = C_{\text{young}} (1 - f_{\text{old}}) + C_{\text{old}} f_{\text{old}} \]  

where \( C_{\text{cal}} \) is the calculated tracer concentration in the sample; \( f_{\text{old}} \) is the fraction of old groundwater; and \( C_{\text{young}} \) and \( C_{\text{old}} \) are the tracer concentrations in the young and old fractions, respectively.

The young fraction (tritium dating scale) of groundwater is transported by an exponential piston flow model (EPM) and the old fraction (radiocarbon dating scale) groundwater is transported by a dispersion model (DM); the mixing fraction was determined using the TracerLPM code (Jurgens et al., 2012). The EPM has been applied to estimate the residence time of young groundwater in the HRB (Chen et al., 2006). Five parameters are adjusted to fit the calculated and measured tritium and radiocarbon concentrations, including mean groundwater residence time of the young and old fractions, the EPM ratio (the ratio of piston flow and exponential flow) required in the EPM, the dispersion parameter used in the DM, and the mixing fraction.

3.4 Groundwater recharge estimation

Recharge in the natural environment on a thousand-year scale is inferred by the radiocarbon and the modern recharge regime affected by irrigation during the past 50 years was evaluated using radiocarbon and tritium data. For the paleorecharge component, recharge rates were calculated using the approach of Harrington et al. (2002) assuming a logarithmic age–depth distribution:

\[ R = \frac{H \theta}{t} \ln\left(\frac{H}{H - z}\right) \]  

where \( R \) is the recharge rate; \( \theta \) is the porosity; \( H \) is the aquifer thickness; \( t \) is the tracer-based groundwater age; and \( z \) is the depth of the midpoint of the well screen below the water table. For the young groundwater component, the position of the peak in the tritium profile is used to estimate the recharge rate, assuming a linear age gradient.

4 Results

4.1 Mountain-block recharge fraction

The primary recharge sources of groundwater in the basin-fill aquifers include river seepage, underflow of groundwater along mountain valleys, and possible lateral flow from mountain blocks. The river and stream waters entering the basins are mostly of CaMgSO₄HCO₃-type, but the TDS concentrations are different in the ZYB and the JQB. The TDS concentration of river water at mountain exits in the JQB is 150–200 mg/L, which is different from the values of 380–600 mg/L in the ZYB (Zhu et al., 2008; He et al., 2012). The lower TDS concentration in the JQB is possibly because of the basin’s relatively small catchment area and lower influence of evaporation on surface waters (He et al., 2012). Mountain-front bedrock springs discharge NaCl-type or NaSO₄Cl-type groundwater of high salinity (TDS 800–6,000 mg/L), and may represent the chemical
characteristics of the MBR water. The mixing of river-seepage water and salty mountain-block water accounts for the current complex groundwater quality distribution in the basin-fill aquifers.

The most common groundwater types in the collected geochemical data are CaMgSO₄, HCO₃ or MgCaSO₄, HCO₃, followed by mixed-cation-SO₄, HCO₃ or mixed-cation-HCO₃, SO₄ (Fig. 2). With respect to cations, Ca-type groundwater dominates in the MFR region and the deep parts of groundwater in the groundwater discharge zone, and mixed-cation types are common in shallow parts of the aquifer (depth <50 m) in the groundwater discharge zone. With respect to anions, HCO₃-dominated groundwater is common in the MFR region and surface water irrigation regions, and can be found at deep parts of aquifers in the valley bottom; whereas SO₄²⁻-dominated groundwater is relatively common in the mountain-front regions of the Yunlu and Longshou Mountains and can be found at shallow aquifers in groundwater irrigation regions (Fig. 3). The mountain-front springs are of NaCl Mixed-cation-SO₄ type (Fig. 2). In the mountain-front region, where the deeper groundwater table is deep (generally >100 m) and agriculture is not developed, the SO₄²⁻ type groundwater is not likely to be the result of fertilizer application. A possible explanation for the presence of this type of groundwater is lateral flow of mountain salty water that intrudes into the river-discharged CaMgSO₄, HCO₃-type fresh water, after which the following cation-exchange reaction can take place (e.g., Appelo and Postma, 2005):

$$Na^+ + 1/2Ca_{X-S} \rightarrow Na-X + 1/2Ca^{2+}$$  (3)

The geochemical models indicate that most groundwater samples in the central ZYB contain 92%–100% river water, confirming a small fraction of lateral groundwater inflow (Table 1). Although the reaction modeling does not provide a unique solution, it at least indicates that the generally accepted groundwater recharge source and flow patterns are chemically reasonable. The calculations suggest that possible mountain block recharge only accounts for less than 5% of most shallow and deep groundwater.

4.2 Mineral-solution equilibria
Calcite, dolomite, and gypsum are important contributors to the Ca²⁺, Mg²⁺, and SO₄²⁻ levels in the groundwater. Groundwater through the basin has variable Mg/Ca molar ratios, mostly between 1:1 and 5:1, reflecting the multiple processes affecting the geochemistry of groundwater, such as incongruent dissolution of dolomite, possible mafic mineral dissolution, calcite precipitation, and cation exchange (Gates et al., 2008; Yang et al., 2011). The deep groundwater in oasis regions is dominated by HCO₃-type and falls on nearly the 1:1 line, whereas shallow groundwater shows variable Mg/Ca ratios. Higher Mg/Ca ratios (>2:1) possibly indicate the dissolution of dolomite or high-Mg-content carbonate (Zhu et al., 2007). The solubility products of calcite, dolomite, and gypsum ($K_{sp}$, $K_{Ca}$, and $K_{Mg}$) are $10^{-8.5}$, $10^{-17.0}$, and $10^{-4.6}$, respectively, at 25°C (Appelo and Postma, 2005). The groundwater

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**Fig. 3.** Groundwater TDS concentrations of the middle reach of the HRB. The groundwater flow direction is inferred from the groundwater-level contours. The groundwater water-level contours are from Geological Investigation Institute of Gansu Province (2002).
Table 1 Summary of average minerals mass transfers and evaporation/dilution factor by hydrochemical zones. Positive mineral mass transfer for dissolution, negative for precipitation; evaporation factor > 0 for evaporation, < 0 for dissolution. Sample locations are shown in Fig. 3.

<table>
<thead>
<tr>
<th>Evolution only</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Gypsum</th>
<th>Na/Ca Ex.</th>
<th>Halite</th>
<th>Albite</th>
<th>K-Spar</th>
<th>CO₂</th>
<th>Na/Mg Ex.</th>
<th>Evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oasis Deep</td>
<td>-0.58</td>
<td>0.34</td>
<td>-0.30</td>
<td>-0.17</td>
<td>0.23</td>
<td>0.25</td>
<td>0.00</td>
<td>-0.11</td>
<td>-0.40</td>
<td>-</td>
</tr>
<tr>
<td>Oasis Shallow TDS&lt;1</td>
<td>-1.10</td>
<td>1.02</td>
<td>0.29</td>
<td>-0.13</td>
<td>0.29</td>
<td>-</td>
<td>-0.01</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oasis Shallow TDS&gt;1</td>
<td>-2.99</td>
<td>3.03</td>
<td>2.27</td>
<td>-1.16</td>
<td>0.74</td>
<td>-</td>
<td>0.05</td>
<td>2.85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gobi Plain TDS&lt;1</td>
<td>-1.73</td>
<td>1.20</td>
<td>0.74</td>
<td>-0.59</td>
<td>-</td>
<td>0.06</td>
<td>0.45</td>
<td>-0.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gobi Plain TDS&gt;1</td>
<td>-4.01</td>
<td>3.09</td>
<td>2.69</td>
<td>-1.71</td>
<td>5.19</td>
<td>-</td>
<td>0.23</td>
<td>3.30</td>
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<table>
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<tr>
<th>Evolution + Mixing (river water % / mountain block water %)</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Gypsum</th>
<th>Na/Ca Ex.</th>
<th>Halite</th>
<th>Albite</th>
<th>K-Spar</th>
<th>CO₂</th>
<th>Na/Mg Ex.</th>
<th>Evaporation</th>
</tr>
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<tbody>
<tr>
<td>Oasis Deep (96.9±5.3)</td>
<td>0.32</td>
<td>-0.24</td>
<td>-0.84</td>
<td>-0.10</td>
<td>-1.12</td>
<td>0.71</td>
<td>0.20</td>
<td>0.48</td>
<td>0.45</td>
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<td>Oasis Shallow TDS&lt;1 (98.5±1.5)</td>
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<td>1.22</td>
<td>0.28</td>
<td>-0.11</td>
<td>0.00</td>
<td>-</td>
<td>0.02</td>
<td>0.80</td>
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<td>Oasis Shallow TDS&gt;1 (86.2±13.8)</td>
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<td>4.11</td>
<td>5.58</td>
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<td>0.38</td>
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<td>-</td>
<td>-</td>
<td>0.17</td>
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<td>-1.11</td>
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<th>Evolution + Evaporation (river water % / mountain block water %)</th>
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<th>Gypsum</th>
<th>Na/Ca Ex.</th>
<th>Halite</th>
<th>Albite</th>
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<th>CO₂</th>
<th>Na/Mg Ex.</th>
<th>Evaporation</th>
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<td>-2.16</td>
<td>0.69</td>
<td>0.62</td>
<td>0.59</td>
<td>0.32</td>
<td>2.00</td>
<td>-</td>
<td>1.16</td>
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<td>-</td>
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<td>-0.16</td>
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<td>3.85</td>
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<td>-</td>
<td>0.05</td>
<td>-0.56</td>
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<table>
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<th>Evolution + Mixing + Evaporation (river water % / mountain block water %)</th>
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<th>Gypsum</th>
<th>Na/Ca Ex.</th>
<th>Halite</th>
<th>Albite</th>
<th>K-Spar</th>
<th>CO₂</th>
<th>Na/Mg Ex.</th>
<th>Evaporation</th>
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<td>-0.02</td>
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<td>-0.28</td>
<td>-1.73</td>
<td>-</td>
<td>0.10</td>
<td>0.13</td>
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<td>0.76</td>
<td>0.19</td>
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<td>0.00</td>
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<td>0.00</td>
<td>2.96</td>
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<td>1.07</td>
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<td>0.22</td>
<td>-1.50</td>
<td>-</td>
<td>0.06</td>
<td>-0.82</td>
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<td>1.59</td>
<td>0.08</td>
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</tbody>
</table>

In the study region, the groundwater residence time of the unconfined aquifers in the oasis regions and the Gobi Plain aquifers, calculations indicate calcite precipitation but dissolution of dolomite and gypsum. A small evaporation factor of 2–4 is generally required in the chemical mass-balance calculation. The consequence of loss of Ca²⁺ in the groundwater is dissolution of small amounts of gypsum accompanied by incongruent dissolution of dolomite. This process is called the dolomitization reaction (Pacheco and Szocs, 2006). Groundwater of SO₄-dominated type becomes common in the Gobi Plain (Figs. 2 and 3). Shallow groundwater in the oasis regions contains both HCO₃⁻-type or SO₄²⁻-type groundwater, and the SO₄²⁻-type groundwater has higher Mg/Ca ratios than deep HCO₃⁻-type groundwater (Fig. 4a), indicating side effects of evaporation. Another alternative process associated with the high Mg/Ca ratio for SO₄²⁻-type shallow groundwater in the oasis that is dolomitization may be driven by anthropogenic effects, as discussed in the following section.
with dissolution of halite and albite.

4.3 High-sulfate water and dedolomitization

Shallow groundwater in the oasis is affected both by canal seepage and irrigation return flow, varying from HCO$_3$-dominated to SO$_4$-dominated (Figs. 2 and 3). The high linear relation between Mg and SO$_4$ (Liu, 2014) is partially related to the overuse of fertilizers containing MgSO$_4$, which causes an increase in the Mg/Ca ratio. Calcium superphosphate (the primary constituent of Ca (H$_2$PO$_4$)$_2$ and CaSO$_4$·2H$_2$O is a widely used phosphatic fertilizer in this region. The considerable amount of CaSO$_4$ introduced by the overuse of fertilizers may also cause dedolomitization (Pacheco and Szocs, 2006). The halite and dolomite levels of lake sediments drilled in a nearby region are high as 17% and 7%, respectively, whereas the gypsum content is as low as 1% (Li et al., 2013). The low gypsum content in the sediments suggests that the dedolomitization in the oasis shallow aquifer may be highly driven by anthropogenic activity. The dedolomitization reaction is described as follows (e.g., Appelo and Postma, 2005):

$$1.8\text{CaSO}_4 + 0.8\text{CaMg(CO}_3)_2 \rightarrow 1.6\text{CaCO}_3 + \text{Ca}^{2+} + 0.8\text{Mg}^{2+} + 1.8\text{SO}_4^{2-}$$  

which forces a Ca/SO$_4$ ratio of 1:1.8 and a Mg/SO$_4$ ratio of 0.8:1.8. If the oversaturation of dolomite is taken into account (average SI$_{ds}$ of 0.3, average SI$_{dl}$ of 0.8 for shallow groundwater in the oasis regions and the Gobi Plain), the Mg/Ca ratio becomes $(K_{ds} + 0.8)/(K_{dl} + 0.3)^2 = 10^{-6.6-0.8}/(10^{-5.5-0.3})^2 = 4$. The high calculated Mg/Ca ratio is supported by the observed high Mg/Ca ratio in the study area (Fig. 4a). The mass transfer alters to

$$5\text{CaSO}_4 + 4\text{CaMg(CO}_3)_2 \rightarrow 8\text{CaCO}_3 + 4\text{Mg}^{2+} + 5\text{SO}_4^{2-}$$  

The Ca/SO$_4$ ratio changes to 1:5 and the Mg/SO$_4$ ratio changes to 4:5, accordingly. Those ratios are observed in the study area (Figs. 5a and b). The lower Ca/SO$_4$ ratio than the theoretical value is caused by the calcite precipitation that is typical of an arid environment. This is confirmed by the observed low Ca$^{2+}$ content in soil salt.
sampled from the Zhangye oasis area, where soil salinization has become a critical problem (Shi et al., 2009). The occurrence of the dolomitization process is supported by the saturation indexes of calcite, dolomite, and gypsum using the sulfite content to monitor gypsum dissolution (Fig. 5c). Most groundwater is saturated or slightly oversaturated with calcite. The saturation index of dolomite is more scattered, and the saturation state of gypsum ranges from undersaturated to equilibrium.

4.4 Origins of groundwater salinity

Shallow groundwater in the discharge zones can have TDS concentrations greater than 1,000 mg/L (Fig. 3). Many studies have ascribed the source of groundwater salinity to evaporation, halite dissolution, and reactions with sedimentary materials (e.g., Edmunds et al., 2006; Gates et al., 2008; Zhu et al., 2008; He et al., 2012). Although evaporitic salt deposits and saline lakes are present in the Gobi plain where local geological conditions prevent groundwater discharge to the river, halite dissolution can be excluded as a significant process considering the absence of halite deposits in the study area and based on the Br/Cl values being lower than the marine ratio (Edmunds et al., 2006; Gates et al., 2008). X-ray diffraction analysis of aquifer materials did not detect significant halite (Li et al., 2013). The Na/Cl ratio of river water in the mountains is 2–4 (Nie et al., 2004); the lower Na/Cl values with increasing Na+ and Cl− ratio (Fig. 6a) is caused by cation exchange that generally happens in relatively more salty water (Zhu et al., 2008). Some groundwater samples with higher Na/Cl ratios (>4) are NaHCO3-type or mixed-cations-HCO3-type, illustrating that the Na levels of these groundwater samples are largely dominated by silicate weathering or ion exchange (Zhu et al., 2008; Wen et al., 2008). The slight linear relation between SO4 and Cl (Fig. 6b) suggests the effects of mineral dissolution on SO4, as described in the two preceding sections. Another potential source of Na+ is weathering of Glauber’s salt (Na2SO4), resulting in Na2SO4-type groundwater, which is only observed in the Gobi Plain (Zhu et al., 2008; He et al., 2012). Glauber’s salt primarily occurs in salty lakes in Yanchi, Gaotai.
Measurements of $^{14}$C of terrestrial tree branches in the Glauber's salt in the west Hexi Corridor indicates that the Glauber's salt was mainly deposited during the last glacial maximum (LGM; Wang et al., 2011). Assuming this salt is a source of Na$^+$ and Cl$^-$, the influenced groundwater would have been recharged after the LGM and will be younger than about 12,000 years.

The relation between $^{18}$O and TDS, however, probably does not indicate significant effects of evaporation (Fig. 7a). Considering the wide range of stable isotope ratios of the river water (Chen et al., 2014), groundwater does not display significant enrichment of heavy stable isotopes (Fig. 7a). Evaporation occurring in water-diversion canals would be quantitatively insignificant relative to the amount of water diverted; flooding irrigation also has little effect in increasing evaporation. Moreover, relatively coarser soil results in a higher percolation infiltration velocity (generally greater than 10 m/d during the irrigation period) in the unsaturated zone (Cao et al., 2002), leaving an insignificant amount of percolation water to evaporate (see also the small evaporation factors in the NETPATH modeling). The salts precipitated during very dry conditions during sediment deposition may be dissolved during the subsequent wetter period (Li and Hao, 1999). Most water samples are offset from the mixing line between groundwater in the recharge zone and the mountain-front bedrock springs. This provides evidence that the mixing of MBR water is not a primary source of salinity. The averaged TDS of river water at the Yingluo Gorge gauging station (YLG) is about 600 mg/L,
about twice that at the Zhengyi Gorge gauging station (ZYG, 340 mg/L); the average runoff at the ZYG is about half of that at the YLG. The salt inputs and outputs of the basins are approximately equal, indicating that the salt balance of the aquifer system is still in an equilibrium state.

In artificial oasis regions, where most irrigation relies on diverted river water, shallow saline groundwater is mixed with fresh river water and irrigation return water, resulting in a TDS concentration of 400–1,000 mg/L (Fig. 3). The effects of irrigation return flow can be identified from the nitrate concentration. Most of the fertilizers utilized in this region are complex nitrate fertilizers, ammonium nitrate fertilizers, phosphatic fertilizers, and potassium fertilizers (mostly KCl and K₂SO₄). The nitrate concentrations in groundwater are relatively lower compared with that in other intensively farmed regions in China (Yang and Liu, 2010). The groundwater NO₃⁻ concentrations in the extensively irrigated Zhangye Basin show a wide range of <1–150 mg/L, with a mean of 26 mg/L (the number of data, \(n = 101\)). Only 24% of collected samples contain NO₃⁻ concentrations exceeding 10 mg/L as N (with a mean NO₃⁻ concentration of 76 mg/L, \(n = 24\)), which is the newly issued drinking water standard in China. In the Jiuxian Basin, where the Gobi is the dominant landscape, groundwater NO₃⁻ concentrations are significantly lower at ~1–40 mg/L, with an average of 11 mg/L (\(n = 36\)). The mixing process is clearly identified by the relation between \(^{18}O\) and nitrate concentration (Fig. 7b).

The relation between tritium and nitrate concentrations (Fig. 8) further suggests three primary end-member groups of water: background groundwater with low NO₃⁻ and tritium concentrations; young water from river and canal infiltration showing low NO₃⁻ but high tritium concentrations; and young irrigation return water with a higher NO₃⁻ concentration and considerable tritium content. Groundwater samples from wells of depth >100 m that have NO₃⁻ concentrations less than 10 mg/L may represent the deep groundwater end-member: these samples generally have TDS of 250–900 mg/L. The relatively young ages of shallow groundwater components indicated by the relatively higher tritium concentrations indicate rapid transport of agricultural chemicals in the aquifer and discharge to the Heihe River. The recycling process of groundwater irrigation generally increases groundwater salinity and nitrate concentration (Plummer et al., 2000). River waters have a low nitrate concentration of 6.1 mg/L (\(n = 14\)). Dissolution with low-NO₃⁻ water diverted from the Heihe River decreases the potential for NO₃⁻ contamination.

5 Discussions

5.1 Mixing of young and old groundwater

The identified three end-members of groundwater is divided into two groups with respect to their distinct time scale: old groundwater recharged in the \(^{14}C\)-dated time scale and young groundwater recharged in the tritium-dated time scale. Tritium and stable isotopes indicate two main groups of groundwater in the study aquifer. The first group is the resident groundwater characterized by a low tritium content (<20 TU) and relatively low stable isotope ratios (\(\delta^{18}O\) of −8.5‰ to −11‰) (Fig. 9). This group of groundwater is sampled from domestic or irrigation wells of depth generally >100 m in the confined parts of the aquifer. This group may originate from snowmelt in high mountains and has a long residence time. The second group consists of mixtures of the first group of groundwater with river leakage and irrigation water diverted from the Heihe River, characterized by a relatively higher tritium content and stable isotope ratios similar to the Heihe River upstream reach (Fig. 9). This group of groundwater is sampled from domestic or irrigation wells of depth generally <100 m in the confined parts of the aquifer. Some of this groundwater type
sampled in wells of depth shallower than 50 m which contains relatively higher nitrate concentrations, suggesting contamination resulting from fertilizer application. Most young groundwater has $^{18}O$ values of $-8.5\%$ to $-6\%\cdot$, indicating the effects of evaporation during the infiltration process.

Tritium and $^{14}C$ in groundwater samples also indicate an extreme mixing process of at least two end-members. In the Zhangye Basin, the tritium concentration (>50 TU) suggests that groundwater was recharged in the 1960s, while a range of 1–15 TU could correspond to mixtures of pre-1950 waters (Qin et al., 2011). However, most groundwater samples that could be identified as bomb peak recharge by $^3H$ have lower $^{14}C$ concentrations of 70–100 pmC (Fig. 9). Without measurements of soil CO$_2$ radiocarbon, an initial groundwater $^{14}C$ concentration of 80 pmC or even lower concentration is commonly used in previous studies (Chen et al., 2006; Zhu et al., 2008; He et al., 2012). The lower initial $^{14}C$ concentration may be related to dedolomitization when groundwater encounters gypsum and dolomite in the unsaturated zone and possible large amounts of Ca and SO$_4$ from irrigation water. Groundwater samples containing $^{14}C$ of more than 100 pmC are post-1950s in age or contain fractions of post-1950s recharge. All these samples contain elevated tritium concentrations. Examples of water containing detectable $^3H$ concentrations (>2 TU) can occur in wells that contain a mixture of water from both old and young sources. Examples of such wells include those that intercept the water table, those are completed with long screens (dozens of meters), and those that are located adjacent to streams.

5.2 Groundwater radiocarbon age determination

The inverse correlation between $^{14}C$ and $^3H$ values (Fig. 10) indicates incongruent dissolution of carbonate aquifer matrix materials, which results in equilibrium isotopic exchange, enrichment of $^{13}C$, and depletion of $^{14}C$ (Gates et al., 2008). The NETPATH calculations indicate that this typically occurs in deep groundwater in the oasis regions. Groundwater sampled from relatively shallow wells (<100 m) and some relatively deep wells with long screens having detectable tritium indicates that the dissolution of calcite is caused by the action of soil CO$_2$. Among these samples, $^{13}C$ evolves to a value of approximately $-7\%$ in an equilibrium state between fresh water and carbonates (Fig. 10). In the deep confined parts of the aquifer, incongruent dissolution continues. However, NETPATH calculations wherein carbon isotopic exchange between calcite and dissolved inorganic carbon produces negative ages in most cases. This suggests that carbon isotopic exchange is probably not an important process.

Additional sources of carbon include CO$_2$ gas, particularly in the shallow unconfined aquifers, and oxidation of organic matter. The calculated partial pressure of CO$_2$ ($P_{CO_2}$) for most groundwater samples exceeds the standard atmospheric value (about 10$^{-3.5}$), but it is lower than the soil value of 10$^{-3.8}$–10$^{-2.0}$ (Chen et al., 2006), indicating that the hypothesis of a closed system in deep aquifers is plausible and carbonate dissolution is still the primary process affecting the DIC concentration. The relatively larger CO$_2$ mass transfers for some shallow wells, especially wells with TDS concentration >1 g/L (Table 1), suggests the re-opening of the system through the groundwater irrigation cycle. The long screen opening in deep wells may also cause gas exchange. Dissolution of more soluble or reactive carbonate, such as aragonite, calcite containing traces of sodium sulfate, magnesium-rich calcite, and dolomite can cause decreases in DIC and increases in $^{13}C$ (Han et al., 2014). The slight increase in $^{13}C$ with decreasing DIC indicates the addition of $^{13}C$-enriched HCO$_3$ from dedolomitization, which causes further increases of $^{13}C$ and a further reduction in DIC. Possible upward deep groundwater leakage and the effects of dedolomitization partially offset the soil CO$_2$ effects in the shallow aquifer.

The $^{13}C$-DIC values of modern water (average $-10.3\%$) are lower than the $^{13}C$ of groundwater with an uncorrected $^{14}C$ age of Holocene (average $-6.6\%$), which may be explained by variations in the relative abundances of C$_3$/C$_4$ plants. Modern desert plants in the HRB are dominated by C$_3$ plants with $^{13}C$ values of $-27\%$ to $-24\%$: C$_4$ plants with $^{13}C$ of $-16\%$ to $-14\%$ account for approximately 6% of total desert plants (Su et al., 2012). Measurements of organic carbon isotopes ($^{13}C_{TOC}$) of lake sediments indicate that C$_3$ plants have dominated since the last glacial period, with $^{13}C_{TOC}$ ranging between $-31\%$ and $-22\%$ (Li et al., 2011; Wang, 2012). Using

![Fig. 10. Relation between $^{14}C$ and $^{13}C$-DIC (the labeled numbers represent well depths relative to groundwater table positions).](image-url)
modern correlations between the relative abundance of C4/C3 plants and climate, Rao et al. (2010) concluded that both temperature and precipitation control the abundance of C4 plants. Qinghai spruce (Picea crassifolia) is the dominant plant in the Qilian Mountains, and has δ13C values between -29% and -25% (Qiang et al., 2003). There was an increase in the abundance of C4 plants during the early Holocene when the monsoon was stronger and the climate became warmer in northwest China (Lu et al., 2012). During the Holocene, because precipitation in the valleys was much higher than at the present day, local precipitation was possibly another important source for groundwater recharge.

5.3 Radiocarbon-timescale recharge

The determined groundwater radiocarbon age profile can be used to estimate the recharge for the old groundwater component. In non-irrigated areas, groundwater age increases logarithmically with depth (Fig. 11a). This distinct trend can be considered to be representative for the recharge area and indicative of spatially distributed recharge, despite the fact that no nested wells are available at single sites to obtain a vertical profile. Applying Equation 1 to the corrected 14C age yields a recharge value of 12 mm/year. The corrected 14C age indicates that most of the recharge occurred between 2,000 and 7,000 years ago, corresponding to the mid-Holocene humid period. The radiocarbon ages of calcareous cementation and the cemented tubes of plants in mega-dunes in Badain Jaran Desert indicates that the climate was more humid in the early Holocene (9.4 kyr B.P.) and at 2 kyr B.P. (Yang, 2000). Old shorelines of ancient lakes also reveal that the lake water levels were higher in the Holocene (Yang and Williams, 2003). The humid period in the Holocene is attributable to the East Asian summer monsoon, the northern front of which may have arrived in this region and brought high precipitation (Yang and Williams, 2003). Large amounts of archeological data for the Neolithic age in China indicate that rain-fed agriculture had extended to the Hexi Corridor during the periods of the Yangshao-Longshan Cultures (7,000–4,000 years B.P.; Fang et al., 1998). According to the water requirements of typical rain-fed millet in that period deduced from current agricultural practice, it is inferred that the precipitation in the Hexi Corridor was 100–200 mm higher than the present-day precipitation (Fang et al., 1998). Although pre-Holocene recharge is also an important source in the deserts north of this region (Gates et al., 2008), the much coarser aquifer materials in the HRB possibly caused the pre-Holocene groundwater to be replenished in the subsequent wet period. At the current hydraulic gradient, the travel time from the MFR zone to the discharge river valleys is about 2–3 kyr. Upward leakage through the confined aquifers is likely to decrease hydraulic velocity and increase the travel time further along path lines into the deep aquifer.

5.4 Tritium timescale recharge

River leakage and irrigation water diverted from the Heihe River during the late 1960s and 1970s must have brought large quantities of tritium into aquifers in the surface water within the irrigation regions. Twelve measurements of tritium in river water sampled in Yingluo Gorge reservoir and the river reach near Zhangye from 2001 to 2003 range from 39 to 78 TU with a mean value of 52 TU (Chen et al., 2010; Qian et al., 2008). The Heihe River originates in a high-altitude area (~3,800 m) in the Qilian Mountains sourced by local rainfall and snow and

![Fig. 11. (a) Groundwater corrected radiocarbon ages in relation to depth below water table and (b) vertical distribution of 3H data. The smooth trend line was derived using the Locally Weighted Scatterplot Smoothing (LOESS) method (Cleveland and Devlin, 1988) to detect the peak in the 3H profile.](image)
ice meltwater, and can receive bedrock groundwater discharge as the base flow before exiting the mountain area. Therefore, the tritium concentration in the Heihe River measured at the MFR zone represents a mixture of high-altitude rainfall and mountain groundwater discharge. According to the tritium concentration variations in rainfall measured at Zhan glye, the tritium concentration in rivers should have been considerably higher during the late 1960s to 1970s than the current values. The tritium concentration in the imported river water can be lowered by radioactive decay, flushing out of the aquifer, or dilution with older groundwater resident in the aquifer (Plummer et al., 2000). Samples with a tritium content of >1 TU are assumed to contain post-1950s recharge. The widespread occurrence of detectable concentrations of $^3$H indicates relatively rapid movement of groundwater in the gravel and sand aquifer. The position of the tritium peak (Fig. 11b) suggests a recharge rate of $\sim$360 mm/year, approximately 30 times larger than the recharge rates derived from the radiocarbon age gradient. The recharge rate indicated by tritium can represent recent changes in the hydraulic conditions of the system, mostly associated with applied irrigation. However, the transition zone between the overlying recent recharge and underlying Holocene and pre-Holocene recharge is not well defined, even at the regional scale across the basin because of wellbore mixing in the long screens of irrigation or monitoring wells. The mean age of the young groundwater fraction is 10–50 years, and the young fractions of groundwater are mostly derived from seepage of canals and irrigation, representing 20%–50% of collected samples.

5.5 Implications for water resources management

Changes in groundwater recharge patterns suggest a potentially quick response of the HRB basin-filled aquifer system to land use change in terms of both quantity and quality. The detection of higher fluoride (exceeding the national drinking water limit) concentrations (He et al., 2013) indicates that salt leaching has contaminated the groundwater. Groundwater pumping lowers the groundwater level and may mitigate soil salinization; however, the irrigation cycle of groundwater would eventually cause agricultural chemical contaminants to accumulate. The percolation of shallow irrigation infiltration into the deeper parts of the aquifers is further enhanced because of absence of continuous low-permeability clay layers. Groundwater age distributions in widely used long-screen public supply wells would determine the response time of the aquifer to different pollutants and help to assess the water supply safety of these wells.

The different time scales of groundwater recharge are primary aspects for model-based water resources management. Most previous modeling efforts have focused on the integration of the surface and groundwater system spatially or the response of the system to climate change and human activities over decadal time scales; nevertheless, rare work has considered the two distinct groundwater recharge time scales together (e.g., Yao et al., 2015; Hou et al., 2014., Wu et al., 2015; Tian et al., 2015). Hydrologic modeling based on only recent hydraulic observations is incapable of capturing the long-term behavior of the system. Determining sustainable groundwater development thresholds using a model-based decision-support system must consider distinct natural and artificial recharge. Groundwater geochemistry data and environmental-tracer-derived hydraulic information can provide important insights to improve those model-based investigations.

6 Conclusions

The evolution of groundwater geochemistry in the middle reaches of the HRB generally reveals a trend from HCO$_3$-dominant to SO$_4$-dominant groundwater in oasis regions and to Cl-type water in the Gobi Plain. Geochemical mass-balance modeling confirms that mixing of lateral mountain-block recharge water is constrained in some local piedmont regions with a small fraction. The geochemical evolution is characterized by dissolution of calcite and dolomite as the primary processes in the deep part of the aquifer, as demonstrated by reaction modeling. In the shallow part of the aquifer, where groundwater has been greatly affected by irrigation, dedolomitization (dolomite re-solution and calcite precipitation) enhanced by the anthropogenic input of Ca and SO$_4$ has become the primary reaction affecting shallow groundwater geochemistry.

The combination of chemical and radioisotope data reveals that groundwater at the depths investigated here (generally shallower than 150 m relative to the water table) can only be explained by a mixture of recently recharged component (on a decadal time scale) and resident groundwater (palcorecharge on a scale of thousands of years). The young groundwater component itself is a mixture of seepage from rivers and canals and irrigation return flow. Calculation using binary mixing models with respect to tritium and radiocarbon reveal that the young groundwater fraction is 20%–50% in those selected groundwater analyses. Dilution with low-$\text{NO}_3$-concentration water diverted from rivers and the relatively short residence time of shallow groundwater in the study aquifer decrease the potential for $\text{NO}_3$ contamination.
However, the potential risk of NO3\textsubscript{3} accumulation in shallow groundwater deserves attention with the knowledge that division water irrigation has been reduced but groundwater irrigation has dramatically increased.

Paleorecharge was relatively small and may have primarily occurred in the mid-Holocene humid period according to corrected radiocarbon ages. Geochemical modeling shows that isotope exchange with soil CO\textsubscript{2} must be taken into account in radiocarbon age correction. Groundwater irrigation has rapidly increased in the past decades, and the highly permeable aquifer in the basin allows the groundwater in the shallow part to function as an open system. The dedolomitization reaction increases δ\textsuperscript{13}C and decreases DIC in groundwater. Additional investigations of radiocarbon ages of groundwater in deeper depths are required. The deep groundwater is not renewable at a meaningful time scale for groundwater management, and mixing with irrigation infiltrates containing high rates of agricultural contaminants is a crucial issue that warrants further investigation.

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