Determination of groundwater recharge mechanism in the deep loessial unsaturated zone by environmental tracers

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HIGHLIGHTS
• We determined groundwater recharge mechanism in thick unsaturated zone covered by loess.
• Both preferential flow and piston flow contribute to groundwater recharge.
• Preferential flow dominates the total recharge.
• The finding has great implication to hydrological modeling.

GRAPHICAL ABSTRACT

Abstract

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1. Introduction

Understanding groundwater recharge mechanism can provide fundamental information for water resources management (Gleeson et al., 2016). However, this is difficult for the regions with thick unsaturated zone or large water storage that increases the complexity of hydrological process dynamics (Camacho Suarez et al., 2015). In such cases, selection of appropriate methods is very important. Although the techniques for groundwater recharge estimation can be classified into physical, tracer and numerical modeling approaches (Scanlon et al., 2002), the tracer technique has been the most successful one in estimating...

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recharge, especially in dry regions (Allison et al., 1994; Gee and Hillel, 1988). Therefore, studying recharge mechanism in regions with thick unsaturated zone using tracer techniques can improve our understanding of groundwater processes.

The Loess Plateau of China, located in a subhumid to arid climate zone, is subject to severe water shortage since significant downward trend has been observed in streamflow and water table (Gao et al., 2015; Liang et al., 2015). Under such scenario, it is very important to understand the hydrological processes to effectively manage water resources. However, the groundwater recharge mechanism has been poorly understood due to the thick loessial soil with a depth up to 250 m (Fu, 1989). It is particularly difficult to investigate groundwater processes on the loess tableland since it is covered by loess over 130 m deep and the water table is >30 m below the surface (Li et al., 2017). As gullies deeply cut through the bedrock, tablelands are isolated as islands. The groundwater should only originate from precipitation since there is no flow from underlying or adjacent aquifers (Yan, 1986). Based on observation of soil moisture and water table, several earlier studies qualitatively concluded that piston flow should contribute little due to the existence of desiccation layers (Li, 1983) while preferential flow might be the dominant recharge mechanism (Wang, 1982; Yan, 1986). However, it is difficult to further quantify the recharge through those conventional methods.

Tracer methods have recently been used for recharge quantification since they can link precipitation with soil water and groundwater, despite the deep vadose zone. For example, Cheng et al. (2014) confirmed that groundwater should be mainly from infiltration of precipitation through rapid flow paths since the isotopic signature of groundwater is similar to precipitation, but different from deep soil water. Although the piston flow in some regions has been quantified by tritium peak and/or chloride mass balance methods in recent years (Gates et al., 2011; Huang and Pang, 2011; Lin and Wei, 2006), little is known about the contributions from preferential flow to total recharge. However, this information is very important for water resource management under the growing pressure of population growth and groundwater depletion.

In this study, we will discuss several questions related to the tracer technique and groundwater recharge in the loess tableland. Is the tracer technique applicable to regions with thick unsaturated zone? Which is the dominant recharge form of groundwater in these regions? How much can groundwater be recharged? This information can be very useful for similar regions with deep depositional environment.

2. Materials and methods

2.1. Study area

The sampling sites are within the Heihe watershed with an area of 1504 km² (a first order tributary of the Jing River) (Fig. 1). The soil is predominantly silt loam with silt contents >50%. According to the observation of six weather stations from 1961 to 2012, the mean annual precipitation is 571 mm with about 55% falling between July and September, and the average annual temperature is 9.4 °C. The land uses includes farmland, forests and grasslands with farmlands occupying >50% of the study area, and rainfed farming is the main form of agriculture due to its limited water resources (Li et al., 2010).

The hydrogeological conditions are quite similar across the study area (Fig. 2). Above the mudstone and sandstone beds (N2 and KZ series), there are three layers of loess cover, i.e. Wucheng Loess (Q1, lower Pleistocene), Lishi Loess (Q2, middle Pleistocene), and Malan Loess (Q3, upper Pleistocene). The Wucheng Loess has a thickness of 22–78 m and is the aquitard due to its low permeability. The Malan Loess is the top soil with a thickness of about 15 m. The depth to water table ranges from 30 to 100 m.

2.2. Sampling and analytical methods

We collected soil samples from seven sites during 2012–2013 to determine soil water contents, chloride concentrations and isotopic compositions (δ18O and δ2H). Among the seven sites, three sites (S1 to S3) were farmlands with a long-term rotation of wheat and maize, two sites were grasslands (S4 from natural grassland and S5 from eight-year-old alfalfa) and the remaining two sites were 20-year old orchards (S6 and S7), respectively. All the sites are flat and have no irrigation, which excludes additional water inputs. The maximum distance between the upstream sampling site and the downstream site is about 100 km. The large distance allows the effect of possible spatial variations due to soil or climate to be considered.

At each site, a hollow-stem auger was used to obtain soil samples at a sampling interval of 0.10 m to a depth of 10 m. Each sample was split into two halves to obtain two sets of samples. For one set, soil water contents were determined by subsampling a composite of two consecutive samples through the oven drying method, thus having a sampling interval of 0.2 m (n = 350). For the other set, a composite of every three consecutive samples was made to obtain two subsamples for the determination of chloride concentration and stable isotopes (n = 210), respectively. The first subsample was used to determine gravimetric water contents by oven drying method, and then 40 g of the dried sample was mixed with 60 ml double deionized water and subsequently agitated for 8 h. Chloride concentration of the supernatant solution was analyzed using ion chromatography (DIONEX ICS-1100, Thermal Fisher Scientific, USA). Chloride concentration of the soil pore water was obtained by dividing chloride concentration of the supernatant solution by the gravimetric soil water content and by multiplying the mass ratio of the solution over the dried soil sample. For the second subsample, soil water was extracted in the laboratory using the vacuum extraction method (Araguás-Araguás et al., 1995; Stewart, 1972) for stable...
isotope measurements. Therefore, Cl concentrations and stable isotope fractions had a sampling interval of 0.3 m for each core.

Precipitation samples were collected at two sites respectively located at the upper and lower reach of the Heihe River, which incorporated the impacts of elevation and climate on isotopic compositions. Precipitation samples in 2012 and 2013 were collected by using a rain gauge. All rainfall water directly flowed into a bottle connected with the funnel, and a pingpong ball was put in the funnel to minimize evaporation. Groundwater was sampled twice per month at seven sites (six for spring and one for well) at proximity to the locations where one or more soil cores were taken. The spring samples were collected at springheads. The well was pumped to let it refill with fresh groundwater before sample collection. The runoff at the outlets of about 10 sub-watersheds was sampled after a wet event during August or September (n = 50, Table 1) to determine the chloride concentration. All precipitation, groundwater and runoff samples were stored in 100-ml polyethylene bottles and refrigerated at temperatures of about 4 °C before analysis. Stable isotopic compositions of the precipitation (n = 123), groundwater (n = 96), soil water samples (n = 210) were determined using an LGR LIWA V2 isotopic liquid water analyzer with a precision of 0.5‰ for δ2H and 0.1‰ for δ18O. Two groundwater samples were taken: One from a well (G7 in Fig. 1) and the other from confined aquifer below the bedrock of unsaturated zone around G4 in Fig. 1. 600 ml groundwater was sampled for electrolytic enrichment before determination by an ultra-low-level scintillation counter (Quantulus 1220, PerkinElmer, Singapore).

2.3. Interpreting groundwater recharge mechanism

2.3.1. Chloride mass balance

As chloride is a conservative element, either at the field or catchment scales, the chloride inputs from atmosphere (P·Clpr) are equal to the sum of those in groundwater (Rtot·Clgw) and runoff (Q·ClQ) (Allison and Hughes, 1978; Dyck et al., 2003; Harrington et al., 2002; Song et al., 2006; Wood and Sanford, 1995).

\[
P·\text{Cl}_{\text{pr}} = R_{\text{tot}}·\text{Cl}_{\text{gw}} + Q·\text{Cl}_{\text{Q}}
\]  

where \(P\) is the mean annual precipitation (mm), \(\text{Cl}_{\text{pr}}\) is the mean annual chloride concentration in precipitation (mg L\(^{-1}\)); \(R_{\text{tot}}\) and \(Q\) are the mean annual total recharge and runoff (mm yr\(^{-1}\)), while \(\text{Cl}_{\text{gw}}\) and \(\text{Cl}_{\text{Q}}\) are the chloride concentration of groundwater and runoff, respectively (mg L\(^{-1}\)).

The total groundwater recharge \(R_{\text{tot}}\) estimated in Eq. (1) may comprise different components. Specifically, if \(\text{Cl}_{\text{gw}}\) (chloride concentration in soil pore water below root zone) is similar to \(\text{Cl}_{\text{gw}}\), piston flow can be assumed as the only recharge mechanism and the recharge rate can be directly estimated by Eq. (1) (Allison and Hughes, 1978). However, if \(\text{Cl}_{\text{gw}}\) is much greater than \(\text{Cl}_{\text{gw}}\), a preferential flow component may exist, and a two-component recharge process should be considered (Sharma and Hughes, 1985; Wood, 1999).

\[
R_{\text{tot}}·\text{Cl}_{\text{gw}} = R_{\text{pf}}·\text{Cl}_{\text{sm}} + R_{\text{pf}}·\text{Cl}_{\text{pf}}
\]  

where \(R_{\text{tot}}\), \(R_{\text{pf}}\) and \(R_{\text{pf}}\) are the total recharge, recharge by piston flow and preferential flow, respectively (mm yr\(^{-1}\)); \(\text{Cl}_{\text{pf}}\) is the chloride concentration in preferential flow.

The contributions of piston and preferential flow to the total recharge can be calculated according to the two-component recharge model as follows:

\[
f(R_{\text{pf}}) = (\text{Cl}_{\text{sm}} - \text{Cl}_{\text{pf}})/ (\text{Cl}_{\text{sm}} - \text{Cl}_{\text{pf}})
\]  

\[
f(R_{\text{pf}}) = 1 - f(R_{\text{pf}})
\]

where \(f(R_{\text{pf}})\) and \(f(R_{\text{pf}})\) are the fractions of piston and preferential flow in total recharge, respectively.

2.3.2. Estimating precipitation-related variables

The precipitation-related variables in Eq. (1) are the mean annual precipitation and chloride concentration in precipitation. The mean annual precipitation can be easily determined from the long-term record of precipitation (over 50 years), and is 571 mm for the period of

---

**Table 1**

Isotopic compositions and chloride concentration in precipitation, groundwater and runoff.

<table>
<thead>
<tr>
<th></th>
<th>δ18O</th>
<th>δ2H</th>
<th>Cl (mg L(^{-1}))</th>
<th>No. of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Precipitation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>−8.1</td>
<td>−56.3</td>
<td>−</td>
<td>123</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>4.1</td>
<td>31.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arithmetic average</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weighted average</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Groundwater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>−10.2</td>
<td>−71.5</td>
<td>4.8</td>
<td>96</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.5</td>
<td>3.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Runoff</td>
<td>−9.2</td>
<td>−67.2</td>
<td>6.3</td>
<td>50</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.9</td>
<td>6.6</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

*Cl concentration in precipitation, estimated from EANET according to the relationships between annual mean precipitation amount and chloride concentration.
the chloride input flux $C_{fl}$ is a key parameter, and it should be determined from an accurate long-term record.

So far, the most reliable data with a ‘long-term’ observation are those from the Acid Deposition Monitoring Network in East Asia (EANET). The data from Jiwozi village near Xi’an city, China (33°50′N, 108°48′E), were used to estimate the chloride inputs at the study site. Located in a rural area, the chloride records in precipitation represent the natural state with little perturbation of atmospheric pollution. About 100 km east of the study area, the annual mean precipitation of Jiwozi is about 573 mm, which is similar as that of the study area (571 mm yr$^{-1}$). Monthly chloride concentrations in precipitation have been recorded from 2001 to 2013. The data completeness is 67% and 51% for 2001 and 2002, and the record of 2003 with complete measurement is greatly deviated from the regressed line of the other years (Fig. 3). The data during 2004–2013 were thus used to estimate a volume-weighted average of chloride concentration as 1.0 ± 0.4 mg L$^{-1}$.

Besides wet deposition, chloride inputs can also be derived from dry deposition and dust. However, the observation of dry deposition cannot be obtained. We, therefore, validated the reliability of the Cl flux by inverse calculation from the recharge rate estimated by tritium peak method. Our previous study showed that tritium contents in soil water were the largest at the depth of 7.2 m (Zhang et al., 2017), and the corresponding diffuse recharge was estimated as 25 mm yr$^{-1}$. Monthly chloride concentrations in precipitation have been recorded from 2001 to 2013. However, the data completeness is 67% and 51% for 2001 and 2002, and the record of 2003 with complete measurement is greatly deviated from the regressed line of the other years (Fig. 3). The data during 2004–2013 were thus used to estimate a volume-weighted average of chloride concentration as 1.0 ± 0.4 mg L$^{-1}$.

2.3.3. Estimating runoff-related variables

The runoff-related variables include runoff amount Q and the chloride concentration in runoff $C_{fl}$. Q was determined by the observation from runoff plots in Changwu Agro-Ecological experiment station starting from 2004. Seven runoff plots have a slope of 0.5°, width of 5 m and length of 20 m or 50 m, with a maize-wheat-fallow rotation. Annually, no more than nine rainfall events generate runoff and the runoff coefficients are 0.015 ± 0.022 (Gan, 2005; Mao, 2012). Therefore, the observed runoff coefficient of 0.015 ± 0.022 was used in this study.

The chloride concentration in runoff on tableland has not been monitored in-situ. However, the runoff at the outlets of about ten sub-watersheds of the Heihe watershed have been sampled in August or September during 2012–2013, and their chloride concentration was determined as 6.3 ± 4.0 mg L$^{-1}$ (n = 50) (Chen, 2015). The chloride concentration in runoff is several times of that in precipitation, which has also been observed in some other catchments (Guan et al., 2010; Peck and Hurle, 1973).

3. Results

3.1. Critical depth for steady state in soil profiles

We firstly used water content, chloride concentration and isotope data from the 10-m soil profiles to identify the critical depth below which tracer concentration are under steady state, so that we can determine the tracer concentration used for piston flow. Soil water contents within the depth of 0–4 m are highly variable for each of the seven soil cores, which could be a result of varying root water uptake and rainfall infiltration (Fig. 4). However, those within the depth of 4–10 m fluctuate around a constant value, indicating reduced seasonal variation of root water uptake and rainfall infiltration. Therefore, the active soil water layers can be defined as the 0–4 m profiles and their thickness across the region seem to be similar.

The average $^{18}$O values of soil water for shallow layers (0–4 m) vary between −12.1‰ and −7.2‰, while those for deeper layers (>4 m) are less variable (between −10.4‰ and −7.7‰) (Fig. 4). The variations among soil profile could be a reflection of evaporation, rainfall infiltration and piston displacement of water over time. Within the
Table 2
Water contents, isotopic compositions and chloride concentration in seven soil profiles.

<table>
<thead>
<tr>
<th>Profiles</th>
<th>Land use</th>
<th>Depth, m</th>
<th>Water contents, %</th>
<th>δ18O, ‰</th>
<th>CI, mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0-10 m</td>
<td>8-10 m</td>
<td>0-10 m</td>
</tr>
<tr>
<td>S1</td>
<td>Farmland</td>
<td>10</td>
<td>18.1</td>
<td>18.6</td>
<td>-8.4</td>
</tr>
<tr>
<td>S2</td>
<td>Farmland</td>
<td>10</td>
<td>16.4</td>
<td>17.7</td>
<td>-7.5</td>
</tr>
<tr>
<td>S3</td>
<td>Farmland</td>
<td>10</td>
<td>17.2</td>
<td>17.6</td>
<td>-10.7</td>
</tr>
<tr>
<td>S4</td>
<td>Natural grassland</td>
<td>10</td>
<td>20.0</td>
<td>20.0</td>
<td>-10.1</td>
</tr>
<tr>
<td>S5</td>
<td>Alfalfa</td>
<td>10</td>
<td>15.7</td>
<td>15.9</td>
<td>-9.6</td>
</tr>
<tr>
<td>S6</td>
<td>Apple orchard</td>
<td>10</td>
<td>15.5</td>
<td>12.9</td>
<td>-9.5</td>
</tr>
<tr>
<td>S7</td>
<td>Apple orchard</td>
<td>10</td>
<td>14.2</td>
<td>13.8</td>
<td>-8.8</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>16.7</td>
<td>16.6</td>
<td>-9.2</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td></td>
<td>2.0</td>
<td>2.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

We directly compared the isotopic compositions and chloride concentration between groundwater and S3, S5–7 are <1‰, while the other profiles have relatively higher δ18O values than groundwater (Tables 1 and 2). However, *t*-test (*p* = 0.05) shows that the isotopic compositions of groundwater are different from those of soil water within the depth of 8–10 m for all profiles except for S7. Chloride concentration in soil is much greater than that in groundwater and precipitation. Therefore, recharge from piston flow cannot be the only source of groundwater. Further, as precipitation and groundwater have similar chloride concentrations, recharge from preferential flow may account for a great proportion of total recharge. In addition, the tritium concentration in the confined groundwater is not detectable while that in the shallow groundwater is 2.5 TU, which confirms the contribution from precipitation.

We carried out dual isotope comparison between precipitation, soil water (>8 m) and groundwater to further analyze their relationships (Fig. 5). Except for a few data points from S3 and S6 profiles are very close to the Local Meteoric Water Line (LMWL), most data points of soil water fall below LMWL (δ2H = 7.36δ18O + 3.59, R² = 0.94), implying that they are from precipitation but enriched by evaporation. The groundwater isotopic compositions are very close to LMWL, suggesting that groundwater may originate from quick precipitation inputs. Furthermore, the isotopic compositions of groundwater are similar to those of precipitation in August and September (Fig. 5).

3.3. Groundwater recharge rates

Based on the observation of chloride concentration, precipitation and runoff amount (Table 1), the regional average recharge can be calculated using Eq. (1) and the uncertainty interval can be given by Eq.
4. Discussion

4.1. Is the mass balance method applicable?

To use the mass balance method, two assumptions related to the steady state in the hydrological system should be validated. The first is related to the steady state between precipitation and groundwater, a prerequisite for Eq. (1) to quantify the recharge rate from precipitation (Leaney et al., 2003; Scanlon et al., 2009). The second is the steady state of chloride concentration in soil water that corresponds only to precipitation input and is free of the impacts from fertilizer application and land use change (Guan et al., 2013; Peck and Hurle, 1973). This forms the basis of Eq. (2) to quantify the recharge rate from piston flow in soil.

Here we used the groundwater tritium concentration in our study and the results of a tritium profile from our previous study (Zhang et al., 2017) to verify the two assumptions. The peak tritium contents corresponding to 1963 precipitation were detected at the depth of 8 m, which implies that modern soil water has not reached water table. For the steady state between precipitation and groundwater, the confined groundwater is tritium free whereas the shallow groundwater has a low but detectable tritium concentration (2.5 TU), which implies that the shallow groundwater consists of post-bomb water. Further, the post-bomb water can only be from precipitation since modern soil water has not reached groundwater (Zhang et al., 2017). The post-bomb groundwater from modern precipitation can be well mixed with the pre-bomb groundwater by the flowpath from the center to the edge of tablelands because of differences in elevation. For the second assumption about steady state of chloride concentration in soil, it can be easily verified by the 8-m depth of peak tritium contents. The 8-m depth suggests that the impacts of fertilizer application and land use change starting in the 1980s on chloride concentration cannot reach 8-m depth; thus, the chloride concentration below 8 m can be considered as steady state.

Subsequently, the chloride concentration below 8 m represents water older than 50 years; thus, it exhibits an age mismatch with that in modern precipitation. To solve this problem, the variability of annual precipitation in the past four centuries on the Loess Plateau was examined. Tan et al. (2014) found that the annual precipitation, controlled by the Asian summer monsoon, fluctuated with time but presented no significant trend over time. As the chloride flux is closely related to the distance from ocean (Hutton, 1976), the long-term average chloride concentration in the precipitation from the Asian summer monsoon would not change. Therefore, the chloride concentration in soil water below 8 m can match that in modern precipitation. Furthermore, the chloride concentration in soil water within the depth of 8–45 m in the study area is 19.2 ± 7.8 mg L⁻¹ (personal communication with Dr. Lu Yanwei). The small variations in the chloride concentration imply that the chloride inputs are stable during the past decades or even centuries. Thus, the age mismatch in the two components of Eq. (2) may not violate the steady state condition.

4.2. Where does groundwater come from?

As the rivers are located in the gullies, with elevations lower than tablelands by several hundred meters, it is unlikely that the groundwater in tablelands is recharged by runoff. Therefore, only two water sources for tableland-groundwater, i.e. precipitation or deep confined water. According to the hydrogeological characteristics, it is highly unlikely that deep confined groundwater flows upward through the thick red clay (22–78 m in thickness, Fig. 2) with low permeability to recharge shallow groundwater, rather than discharging directly to lower gullies (Tan et al., 2016). This conclusion is confirmed by the groundwater tritium contents in our study since groundwater from the confined aquifer is tritium free while the shallow groundwater has detectable tritium content. Further, the water table responded to rainy season with an increase of about 0.3 m in Changwu tableland within our study area (Wang et al., 2010). Therefore, local precipitation is likely the recharge source for groundwater in shallow loess aquifers.

The feasibility of precipitation to recharge groundwater through the deep unsaturated zone is still highly debatable; therefore, it is necessary to determine how precipitation recharges groundwater. Our results show that groundwater is likely to be from episodic recharge during August and September. This conclusion is consistent with the progressive understanding of groundwater recharge in literature. Lin and Wei (2006) found that the soil water below 15-m depth was almost tritium free while the groundwater with a water table of 20–30 m deep has a tritium content of 34.4–43.4 TU, suggesting piston flow was not the only recharge mechanism. Gates et al. (2011) concluded that drainage through the unsaturated zone contributed little to spring discharge in the Zhifangou Catchment due to the distinct isotopic signatures between spring water and soil pore water. Furthermore, Tan et al. (2016) observed that the groundwater isotopic compositions had a
clear response to precipitation in rainy season in Gansu Province, which is very close to our study area.

The groundwater is thus likely from local precipitation by preferential flow, which can be further validated by the tritium content in groundwater. The groundwater from pre-bomb events should be tritium free; however, the results from this study as well as those distributed widely across CLP contradicted this assumption. Specifically, the tritium contents >10 TU have been detected in the other regions (Huang et al., 2014; Lin and Wei, 2006; Liu et al., 2009; Ma et al., 2006; Su et al., 2009; Tan et al., 2016). In this study, the tritium contents are very low though preferential flow dominates groundwater recharge. This controversial issue can be interpreted by the sharp comparison between the small recharge and huge water storage in the thick aquifer. Assuming groundwater as a well-mixed reservoir (Le Gal La Salle et al., 2001), the long-term averaged renewal rate is 0.2% per year based on the tritium data. Therefore, the percentages of modern groundwater from the past 50 years should be about 10%, and the large groundwater storage dilutes the tritium concentration. Furthermore, the high concentration of precipitation tritium around 1963 has gone through radioactive decay that substantially reduces the tritium contents from bomb water and the tritium contents in modern precipitation are low.

The identified recharge mechanism is similar as regions covered by loess in other countries. For example, the ~8 m depth tritium and nitrate profiles across two loess hillslopes exhibit multiple peaks in Pullman in southeastern Washington State, USA, which indicates that piston flow is not the sole flow process, and further simulation indicated that deeper peaks resulted from preferential vertical and/or lateral flow (O’Brien et al., 1996).

### 4.3. How much is groundwater recharged?

The estimated total recharge rate falls within the ranges from literatures for the Loess Plateau (9–100 mm yr⁻¹, 2–22% of average annual precipitation, Table 4). However, the recharge rates from the earlier work are mostly in form of piston flow, while those in this study are the sum of piston and preferential flow. The estimated piston flow in this study is about 14 mm yr⁻¹, accounting for 2% of mean annual precipitation (calculated from Table 3) and 13 ± 4% of the total recharge. These values are smaller than most of the earlier work using tracer method (9–100 mm yr⁻¹, Table 4); however, they are very close to those based on numerical models. For example, Huang and Gallichand (2006) estimated the deep percolation for farmland and apple orchard as 9.3–18.3 mm accounting for 2–3% of mean annual precipitation, and Zhang et al. (2007) simulated the deep percolation for farmland as 17 mm accounting for 3% of mean annual precipitation. This may be because the two modeling studies only considered piston flow and the similar values imply that the estimated recharge for piston flow in this study is reliable.

The above differences may be due to the following two reasons: First, the chloride concentration in precipitation used by earlier work is greater than this study (1.0 mg L⁻¹), such as 1.7 mg L⁻¹ or 1.4 mg L⁻¹, which are also estimated from EANET without excluding the incomplete observation (missing values). Annual estimates of volume-weighted Cl concentration from incomplete observation could be biased considering the strong variability in the monthly Cl concentrations in the precipitation. It is prudent to exclude, in the calculation of mean annual Cl concentration, those years with >10% missing values.

Second, after comparing the chloride and isotope in precipitation, soil water and groundwater, preferential flow was taken into account and the two-component mass balance method was used. However, most of earlier studies did not incorporate groundwater as a variable in the mass balance equation, and directly calculated the recharge based on methods for piston flow. The techniques only based on unsaturated-zone data provide estimates of potential recharge, whereas those based on groundwater data generally provide estimates of actual recharge (Scanlon et al., 2002). Therefore, by incorporation of groundwater, the results of this study likely reflect the actual values.

### 4.4. What is the implication to groundwater recharge monitoring and modeling?

This study has important implication for groundwater recharge monitoring and modeling in the region. A vadose zone deeper than 30 m is very common on the Loess Plateau and in many parts of the world. As a result, there is a huge volume of available water storage in the vadose zone. Normally, we assume all the water participates in transport, and transit time (or residence time) can be calculated as the time it takes to replace all the water in the vadose zone. By measuring soil water contents within the vadose zone, we could estimate soil water storage in the zone. Given the deep drainage rate, we can calculate the residence time or transit time of water and chemicals within the zone. As demonstrated

### Table 4

<table>
<thead>
<tr>
<th>No</th>
<th>Location</th>
<th>Methods</th>
<th>Land use</th>
<th>Isotope slope Cl concentration, Piston recharge</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P G S</td>
<td>mm yr⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>Zhifangou</td>
<td>CMB &amp;</td>
<td>Five sites: two farmlands, one tree plantation, one hillside with introduced shrubs, one natural forest L⁻¹</td>
<td>500</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Catchment, Shaanxi</td>
<td>Isotope</td>
<td>vegetation</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>Heqian, Guyuan</td>
<td>CMB &amp;</td>
<td>Five sites: two natural grasslands, two farmlands, one alfalfa</td>
<td>450</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Isotope</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>Wudan, Inner Mongolia</td>
<td>Tritium profiles</td>
<td>No vegetation</td>
<td>360</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>Pingdeng, Shaanxi</td>
<td>Tritium profiles</td>
<td>No vegetation</td>
<td>550</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Xifeng, Gansu</td>
<td>CMB</td>
<td>Winter wheat</td>
<td>523</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>Changwu, Shaanxi</td>
<td>Modeling</td>
<td>Apple orchard and wheat</td>
<td>545</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>Luochuan, Shaanxi</td>
<td>Modeling</td>
<td>Farmland</td>
<td>568</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>Helhe watershed, Gansu &amp; Shaanxi</td>
<td>CMB &amp;</td>
<td>Seven sites: three farmlands, two grasslands and two apple orchards</td>
<td>584</td>
<td>7.4</td>
</tr>
</tbody>
</table>

P, precipitation; G, groundwater; S, soil water; R, recharge. Isotope slopes of precipitation in study 1 and 2 are all from Xi’an City.
by Edmunds and Smedley (2000), the transit time can be as long as hundreds to thousands of years. However, if the available storage is probably bypassed through active preferential flow system, the calculated transit time would be erroneous, substantially underestimating water renewal and surface-applied chemical arrival time at the ground water. This would also invalidate the conventional methodology for monitoring and modeling the hydrologic system. New paradigms of monitoring and modeling the hydrologic system may be required in the thick vadose zone.

Though the recharge in this thick unsaturated zone is mainly from preferential flow, the pathway and the trigger are poorly understood. Most groundwater recharge models assume that recharge is predominately piston flow in arid and semi-arid zones. Performing well for regions where piston flow dominates, those models may fail for preferential flow-dominated recharge regions. Some models do take preferential flow into consideration; however, their treatment of the preferential flow is largely empirical, making it difficult to extrapolate the model results in space and time. Therefore, the key issue for a model is to quantify the piston flow under all land use and to determine the threshold for precipitation to generate preferential flow. For the latter, when and how does water flow through macropores should be fully understood to parameterize the model (Beven and Germann, 2013; Nimmo, 2012).

5. Conclusion

Environmental tracer methods including stable isotopes and chloride balance methods were used to interpret the relationships among precipitation, soil water and groundwater in the tableland of China’s Loess Plateau. The isotopic compositions of groundwater were different from precipitation, soil water and groundwater in the tableland of China. The isotopic compositions of groundwater were different among regions with different preferential flow recharge forms and quantification in regions with depositional environment. The identified recharge rate on the Loess Plateau with different land use and to determine the steady state of soil water at depth are valid, and the vadose zone provide useful information for groundwater management and recharge modeling.

Conflict of interest

The authors declare that they have no conflict of interest.

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