HYDROLOGICAL PROCESSES
Hydrol. Process. **27**, 1238–1252 (2013)
Published online 17 April 2012 in Wiley Online Library
(wileyonlinelibrary.com) DOI: 10.1002/hyp.9302

Soil profile evolution following land-use change: implications for groundwater quantity and quality

Tianming Huang,[1] Zhonghe Pang[1]* and W. Mike Edmunds[2]

[1] *Key Laboratory of Engineering Geomechanics, Institute of Geology and Geophysics, , Chinese Academy of Sciences, PO Box 9825, Beijing 100029, China*
[2] *Oxford University Centre for Water Research, School of Geography and the Environment, , Oxford University, South Parks Road, Oxford OX1 3QY, UK*

Abstract:

Soil and vadose zone profiles are used as an archive of changes in groundwater recharge and water quality following changes in land use in an area of the Loess Plateau of China. A typical rain-fed loess-terrace agriculture region in Hequan, Guyuan, is taken as an example, and multiple tracers (chloride mass balance, stable isotopes, tritium and water chemistry) are used to examine groundwater recharge mechanisms and to evaluate soil water chloride as an archive for recharge rate and water quality. Results show that groundwater recharge beneath natural uncultivated grassland, used as a baseline, is about 94–100 mm year^{-1} and that the time it takes for annual precipitation to reach water table through the thick unsaturated zone is from decades to hundreds of years (tritium free). This recharge rate is 2–3 orders of magnitude more than in the other semiarid areas with similar annual rainfall but with deep-rooted vegetation and relatively high temperature. Most of the water that eventually becomes recharge originally infiltrated in the summer months. The conversion from native grassland to winter wheat has reduced groundwater recharge by 42–50% (50–55 mm year^{-1} for recharge), and the conversion from winter wheat to alfalfa resulted in a significant chloride accumulation in the upper soil zone, which terminated deep drainage. The paper also evaluates the time lag between potential recharge and actual recharge to aquifer and between increase in solute concentration in soil moisture and that in the aquifer following land-use change due to the deep unsaturated zone. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS groundwater recharge; land-use change; chloride mass balance; Loess Plateau of China; soil profile

Received 24 October 2011; Accepted 2 March 2012

INTRODUCTION

The study of the impacts of climate change and anthropogenic activities on water resources has been a hot topic over the past decade. It has been suggested by Meybeck and Vörösmarty (2004) that the global impact of direct human intervention in the terrestrial water cycle (through land-use change, urbanization, industrialization and water resources development) is likely to surpass that of recent or anticipated climate change, at least over decadal time scales. In sub-humid to arid areas, the total global groundwater depletion has increased from 126 km^3 a^{-1} in 1960 to 283 km^3 a^{-1} in 2000 owing to increased groundwater abstraction, especially in the world's major agricultural regions, including northwest India, north China and the central USA (Wada *et al.*, 2010). Furthermore, in agricultural areas, excessive use of fertilizers has directly or indirectly affected the groundwater quality (Böhlke, 2002). Land-use change is also a significant factor affecting groundwater recharge and water quality in agriculture regions (Scanlon *et al.*, 2005).

In the past 300 years, cultivated cropland and pastureland have increased globally by 460 and 560%, respectively (Klein Goldewijk, 2001), and past land-use changes have greatly impacted global water resources (Scanlon *et al.*, 2007a). Whereas studies of land-use change have mainly focused on climate and habitat loss on biodiversity (DeFries and Eshleman, 2004), the study of anthropogenic land-use change on water resources has received less attention (Lambin *et al.*, 2002; Scanlon *et al.*, 2005) especially impacts on groundwater and its recharge (Scanlon *et al.*, 2010).

Changes in land use, particularly transitions between grasslands and forests, have potentially large impacts on water balance and salt fluxes in the ecosystem (e.g. Jobbágy and Jackson, 2004; Stonestrom *et al.*, 2009). This is mainly due to the differences in evapotranspiration for different vegetation (Zhang *et al.*, 2001) and root system (Calder, 1998; Jobbágy and Jackson, 2004). A typical example from south-western Niger shows that the water table has been rising in the past decades (from 1963 to 2007 by 4 m) as a result of land clearing (from natural bush to millet), leading to an increase in groundwater recharge from the previous 2–5 mm year^{-1} to the present 20–25 mm year^{-1}, despite an ~23% deficit in monsoonal rainfall from 1970 to 1998 (Leduc *et al.*, 2001; Favreau *et al.*, 2009). Some other examples from Australia (e.g. Allison *et al.*, 1990; Cook *et al.*, 2004; Silburn *et al.*, 2009), south-western USA (e.g. Scanlon *et al.*, 2007b) and central Argentina (Santoni *et al.*, 2010) show that the conversions from natural ecosystems to rain-fed agriculture have increased groundwater availability through enhanced recharge. Conversely the change from arable agriculture to woodland or other high water demand

*Correspondence to: Zhonghe Pang, Institute of Geology and Geophysics, Chinese Academy of Sciences, No. 19, Beitucheng West Road, Chaoyang District, Beijing 100029, China.
E-mail: z.pang@mail.iggcas.ac.cn

vegetation in many European countries have caused increased evapotranspiration (Wattenbach *et al*., 2007) and decreased groundwater recharge (Zhang and Hiscock, 2010) based on soil moisture models. Improved understanding of groundwater recharge then can help to provide valuable information on the history of land-use change and for developing sustainable groundwater resources programmes (Scanlon *et al*., 2006).

In the aforementioned semiarid study areas, the native vegetation is mainly deep-rooted vegetation, e.g. eucalyptus mallee in Australia (Allison *et al*., 1990), shortgrass prairie in south-western USA (Scanlon *et al*., 2009), dry forests in central Argentina (Santoni *et al*., 2010) and natural bush in South-west Niger (Leduc *et al*., 2001). The deep-rooted vegetation and evapotranspiration matching rainfall inputs lead to negligible deep drainage. However, in the Loess Plateau of China (LPC), native vegetation cover for the area with loess is grassland environment (herbaceous vegetation) of the shallow rooted (Liu, 1985; Li *et al*., 2003). A series of unsaturated zone profile information from Africa, north China and other (semi)arid parts of the world (Edmunds, 2010) shows that any single location recharge rates are highly variable for a given amount of rainfall, soil type and thickness as well as vegetation cover. When they are all in semiarid areas with similar annual rainfall, it is worth to compare the differences in groundwater recharge rate and the effects of land-use change.

Because of the high evapotranspiration (small evapotranspiration uncertainties result in large recharge uncertainties) and uncertainty of simulation parameters, the conventional water balance and Darcy flux measurements usually involve large errors in recharge estimation for (semi) arid areas (Edmunds and Walton, 1980; Gee and Hillel, 1988; Allison *et al*., 1994). Neither can artificial tracers give useful results during the short period of measurement (Walker *et al*., 1991). Geochemical tracer methods, e.g. tritium (Smith *et al*., 1970), chloride (Allison and Hughes, 1978; Edmunds and Walton, 1980) and chloride-36 (Phillips *et al*., 1988) in unsaturated zone, have been most successful in estimating groundwater recharge rate in (semi) arid areas (Allison *et al*., 1994). A more generalized chloride mass balance (CMB) is given by Ginn and Murphy (1997), which allows for time-varying Cl deposition for applications where these inputs are well characterized. The results obtained by the CMB compare well with the independent recharge estimates obtained from tritium peak analysis in many sites, e.g. north-western Senegal with precipitation of 290 mm year^{-1} (Gaye and Edmunds, 1996), Cyprus with precipitation of 410 mm year^{-1} (and this is a coastal site also where there could have been an aerosol addition; Edmunds *et al*., 1988), Gambier Plain in Australia with precipitation of 700–750 mm year^{-1} (Allison and Hughes, 1978). Scanlon *et al*. (2006) made a synthesis of global groundwater recharge estimations in (semi)arid areas and pointed out that the CMB technique is now widely and generally successfully used to estimate groundwater recharge.

For the estimation of changes in groundwater recharge, water level measurements, the most direct evidence of impacts of land-use change on groundwater recharge (Healy and Cook, 2002; Favreau *et al*., 2002; Scanlon *et al*., 2005), cannot be used when long-term groundwater level monitoring records are unavailable and when the groundwater level is affected by pumping, which can mask any impact of land-use changes (Scanlon *et al*., 2007b).

Unsaturated zone solute profiles play an important role in studying the impacts of groundwater recharge, and some previous studies have used chloride profiles to confirm increased groundwater recharge (e.g. Walker *et al*., 1991; Scanlon *et al*., 2007a) and degraded water quality (Allison *et al*., 1990; Leaney *et al*., 2003; Scanlon *et al*., 2009) as a consequence of land-use change.

The LPC is one of the most severe areas of soil erosion in the world. Over 60% of the land in the LPC has been subjected to soil and water loss (Yang and Yu, 1992), and the sediment load of the Yellow River has 9–21 times more solid particles content than that of most major rivers in the world (Shi and Shao, 2000). Since the 1950s, governments began soil and water conservation practices to control the soil erosion and increase the productivity of crops. Alfalfa, trees and shrubs have been widely employed for ecological restoration, instead of wheat. However, since the 1980s, a more negative water balance and hence drier soil has occurred, as a result of the introduction of alfalfa, trees and shrubs, combined with a long-term low rainfall period (Chen *et al*., 2008). Studies from selected catchments in the LPC following large-scale soil conservation measurements show decreases in surface runoff (Huang and Zhang, 2004; Mu *et al*., 2007; Zhang *et al*., 2008).

The impacts of land-use change on groundwater resources in the area have received little attention. Studies of groundwater recharge were mainly implemented in the 1970–1980s and focused on loess plains (e.g. Xifeng and Luochuan) by using simple water balance measurements and showed that the groundwater recharge were 33–94 mm year^{-1} or 6.7–15% of the mean annual precipitation (Qu, 1991). They also pointed out that precipitation is the main recharge source to groundwater. However, Chen *et al*. (2011) commented that the main source of recharge of the groundwater in the Ordos Plateau (on the north of the LPC) and that the LPC is not the local precipitation, as the mean isotopic compositions of the local precipitation are significantly higher than those of groundwater. Significant work using tritium profiles (Zhang *et al*., 1990; Lin and Wei, 2006) shows that the groundwater recharge accounts for 12–13% of the annual precipitation. Most recently, Huang and Pang (2011) used two soil chloride profiles (G1 and G2-1) in Hequan, Guyuan, Ningxia Province, and two (X1 and X2) in the Xifeng loess plain, Gansu Province, both in the central LPC to demonstrate that the CMB is admirably suited to investigating recharge processes in loess. They also modified the standard soil CMB approach for recharge estimation so that it can potentially be applied in situations where recharge has been lowered following a land-use/land-cover change. Gates *et al*. (2011) pointed out that mature tree and shrub plantations prevent deep drainage. Yin *et al*. (2010) used the CMB approach between precipitation and groundwater to estimate groundwater recharge rate in the Ordos Plateau (on the north of the LPC) with precipitation of less than 400 mm year^{-1}. Yin *et al.* (2011b) used multiple methods for estimating groundwater recharge in the Ordos Plateau and pointed out that there was no consistent bias with any of the methods.

This paper aimed at improving our understanding of the mechanism of groundwater recharge in loess as well as groundwater evolution (quantity and quality) following land-use change. The specific purpose of this study is to

1. investigate the groundwater recharge rates, ages and mechanisms by using relatively deep soil profiles and multiple tracers (^{2}H, ^{18}O, ^{3}H, CMB and water chemistry) in Hequan, Guyuan, a typical loess-terrace agricultural region in the LPC,
2. evaluate chloride profiles in unsaturated zone moisture as an archive of changes in groundwater recharge and water quality following land-use change in (semi)arid areas and
3. assess the time lag between potential recharge and actual recharge and between increase in solute concentration in soil moisture and that in the aquifer.

METHODS

Assuming that the only source of chloride is atmospheric (rainfall or dry deposition) and that there is no contribution of chloride from weathering, the surface runoff is negligible, and one-dimensional vertical steady-state chloride flux is tenable, the recharge rate (R) is given by (Allison and Hughes, 1978; Edmunds and Walton, 1980)

$$R = \frac{P \cdot C_p}{C_{us}} \quad (1)$$

where P is the precipitation, C_p is the chloride concentration in bulk precipitation (including wet and dry fallout) and C_{us} is the chloride concentration below the depth of the root zone (Zr) to the available sampling depth. This represents potential recharging pore water (Edmunds *et al.*, 1988). Because of the high cost and difficulties associated with the collection of wet and dry depositions separately, bulk precipitation is often the only technique employed in most studies for the quantification of atmospheric deposition (Allison and Hughes, 1978; Dettinger, 1989).

Following land-use change (e.g. tree planting) that leads to decreased groundwater recharge, the only factor that changes is the increased evapotranspiration of the vegetation. As plants exclude chloride during evapotranspiration, increased evapotranspiration will result in increased chloride content in the soil profile (Scanlon *et al.*, 2007a). Before a new equilibrium for the whole unsaturated zone is established, the decreased recharge will lead to a zone of chloride accumulation within certain depth. Assuming that there is a depth, Zb, at which the chloride concentration remains at the value of old land use, the chloride contents above Zb represent new land use and below Zb represent old land use. When a steady-state condition under new land use has been established above Zb and below Zr (Walker *et al.*, 1991), the absolute change in groundwater recharge (ΔR) is given as (Huang and Pang, 2011)

$$\Delta R = R_n - R_o = \left(P \cdot C_p + D\right)\left(\frac{1}{C_{sn}} - \frac{1}{C_{so}}\right) \quad (2)$$

and the relative changes is given as

$$\frac{R_o - R_n}{R_o} = 1 = \frac{C_{so}}{C_{sn}} \quad (3)$$

where R_o is the recharge rate under the condition of old land use, R_n is the recharge rate under new land use, C_{so} is the average chloride concentration in old land use above the depth of Zb derived from new land use and C_{sn} is the average chloride concentration in new land use above Zb. As the concentration of Cl in soil profile is inversely proportional to recharge rates, the precision of the estimate will increase with decreasing recharge rate (Allison *et al.*, 1994), and the estimation of decreased groundwater recharge following land-use change is more reliable than the estimation of increased recharge rate (Gee *et al.*, 2005).

Once the soil moisture/solutes reach the water table following new land use, the solute concentration in groundwater begins to change. The change in the concentration of solute depends upon the concentration of the solution entering the aquifer (C_{in}), the new aquifer recharge rate (q), the initial solute concentration of shallow groundwater (C_o) in the aquifer and the amount of water in the aquifer (porosity, n; thickness of the aquifer, H). Assuming that the water in the aquifer is well mixed, that the discharge from the aquifer is equal to the recharge and that the aquifer is a steady-flow system, the mass balance equation describing the time variation of the average concentration in the aquifer is given by (Appelo and Postma, 1993)

$$nH\frac{\partial C}{\partial t} = -q(C - C_{in}) \quad (4)$$

Solving the aforementioned differential equation for an initial concentration of C_o yields

$$C(t) = C_o e^{-qt/nH} + C_{in}\left(1 - e^{-qt/nH}\right) \quad (5)$$

where $C(t)$ is the average concentration in the aquifer at time t.

Stable isotopes (^{2}H and ^{18}O) are also used here semiquantitatively to determine sources and mechanism of recharge. Tritium is one of the most important transient and ideal tracers used in hydrological research. Environmental tritium, introduced into the hydrological cycle by atmospheric thermonuclear testing in the 1950s and 1960s, provides a useful tracer for water originating from this period (Smith *et al.*, 1970). The tritium peak approach has now become obsolete in most regions of the world because of its short half-life of 12.32 years, hydrodynamic dispersion, and high recharge rates or shallow water tables. In some places, however, the tritium peak can still be detected, e.g. a tritium peak of 230–235 TU in Chinese deep unsaturated loess in 1997 and 1998 (Lin and Wei, 2006) and 64 TU in deep unsaturated loess in Alsace, France, in 2002 (Baran *et al.*, 2007). This study will measure the tritium content in groundwater to distinguish modern water from pre-modern water. On the basis of tritium input data from Ottawa in Canada (1953–2007) and Yinchuan (1988–2000) and Xi'an (1985–1993) in the LPC (IAEA and WMO, 2009), groundwater with tritium content less than 1 TU (sampling time is 2009) can be considered as pre-modern water (before 1952).

STUDY AREA, SAMPLING AND ANALYSES

Loess is an aeolian sediment formed by the accumulation of wind-blown silt and lesser and variable amounts of sand and clay over some 2.4 Myr (Liu, 1985). Loess is homogeneous, porous, friable, pale yellow or buff, slightly coherent, typically non-stratified and often calcareous. The material composition of loess around the world (such as the Yellow River Basin, Central Asia, Eastern Europe, Western Europe and Northern America) is similar (Liu, 1985). Silt (0.05–0.005 mm) accounts for a significant part (50–80%). Chinese loess is mainly distributed in the middle reaches of the Yellow River (Figure 1), accounting for about 72% of the loess-covered area in China (0.44 million km^2).

The study site, the Hequan terrace, Guyuan, Ningxia Province, is located in the east of the Liupan Mountains in the central LPC. As recorded by the Guyuan Meteorology Station, the average precipitation from 1957 to 2008 was 450 mm year^{-1}, the annual potential evapotranspiration was 1330 mm year^{-1} and the average temperature was 6.6 °C. About 60% of the annual precipitation falls between July and September (Figure 2) during the Asian summer monsoon.

Clayey sand and gravel is overlain by upper Pleistocene Loess (Malan Loess, Q_3) in Hequan (Figure 1). There is no surface runoff on the terrace in the study area. The water table [elevation = 1795–1815 m above sea level (a.s.l.)] is higher than the streams (elevation = ~1785 m a.s.l.), so the stream contributes little to the aquifer.

The vegetation cover has now been extensively modified by intensive artificial agriculture in most terraces and loess plains. It is very difficult to find an area of loess where no disturbance/cultivation has taken place, but two sites of natural grassland at the high segment of the toposequence in Hequan, Guyuan, have not been disturbed for at least 100 years when land development commenced, according to our investigation. Almost all the land has been converted to winter wheat (~90%) with a current average grain productivity of ~2200 kg ha^{-1} year^{-1}, and alfalfa (8–9%) covers most of the remaining area. This provided a good opportunity to study the groundwater recharge evolution and groundwater quality change following land-use change.

Soil samples were collected from five profiles in Guyuan (Table I), which represent a long-term land-use change setting. Profiles G1 (depth = 14.25 m, natural land of sparse grass) and G1-2 (depth = 7 m, natural land of sparse grass) are used to provide a baseline land-use profile. Profiles G2-1 (depth = 11.25 m) and G2-2 (depth = 18.25 m) represent a 100-year-old winter wheat

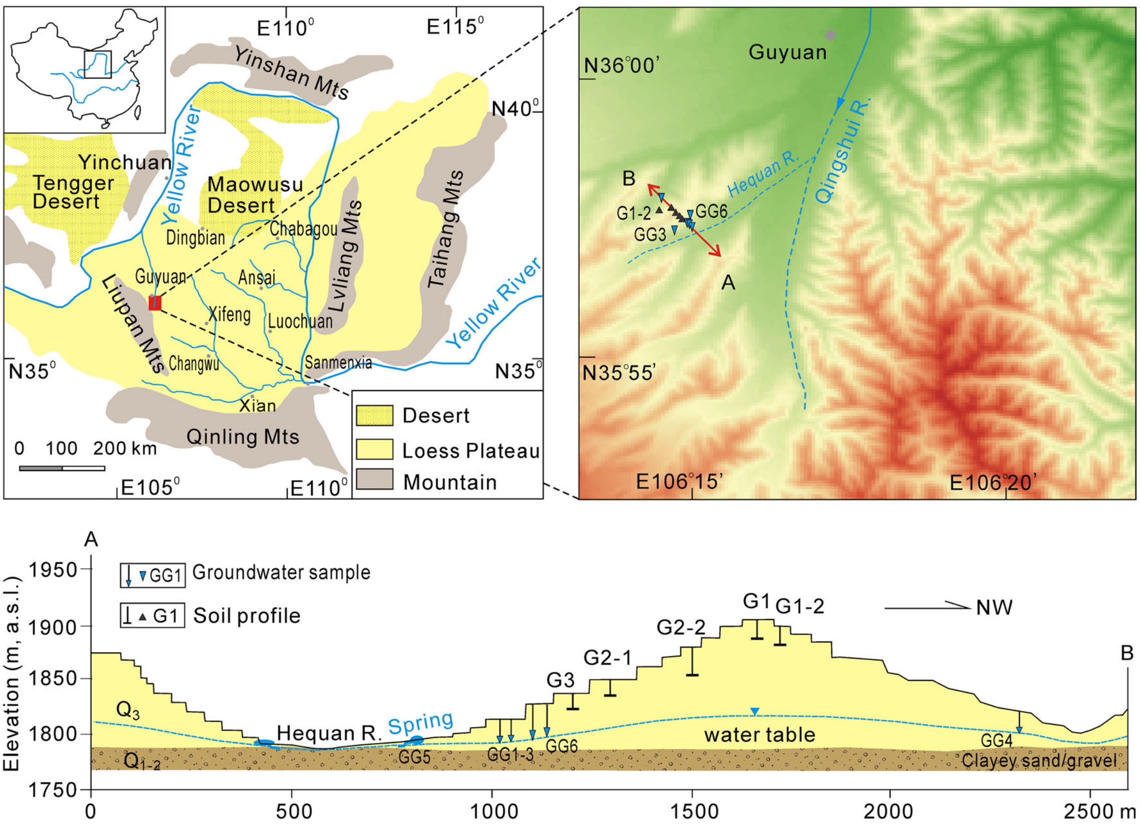

Figure 1. Study area and hydrogeological section of Hequan, Guyuan, and sampling sites

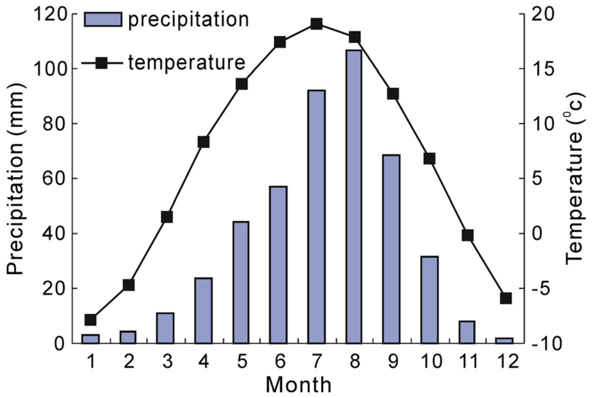

Figure 2. Monthly precipitation and temperature distribution in Guyuan

field. Profile G3 (depth = 7 m) represents a 30-year-old alfalfa (*Medicago sativa*), formerly a winter wheat field.

Chloride data of G1 and G2-1 have been published in a previous paper (Huang and Pang, 2011). G1-2 and G2-2 are drilled for study variation of chloride distribution in the same land use. Soil moisture was exacted from two deep profiles (G1 and G2-2) to study groundwater recharge mechanism. G3 is for new land-use type (alfalfa), which is one of the main land-use conversions in the LPC.

The soil samples were obtained using a hollow-stem hand auger or/and a Luoyang spade with interchangeable 1.5 m aluminium rods. Bulk soil samples of ~400 g were collected at intervals of 0.25 m. Samples were immediately sealed in polyethylene bags. Gravimetric moisture content (θg) was determined by drying a minimum of 80 g of soil at 110 °C for 12 h. To determine the Cl concentration, double-deionized water (40 ml) was added to the oven-dried soil sample (40 g). Samples were agitated intermittently for 8 h. The supernatant solution was filtered through 0.45 μm filters. Solutes were then analysed by ion chromatography. The Cl concentration of the soil solution was then calculated by dividing the measured concentration by the gravimetric moisture content and by multiplying the mass ratio of the solution over the oven-dried soil sample.

For stable isotopic analysis, soil moisture for profiles G1 and G2-2 was extracted using azeotropic distillation (Revesz and Woods, 1990) with a reported accuracy of ±2‰ for δ^2H and ±0.2‰ for δ^{18}O. Resulting samples were collected in glass vials, and a few grams of paraffin wax were added to the vials to remove remaining traces of toluene. Before extracting from field samples, tap water was added into three oven-dried loess samples, forming moisture content of 5, 15.6 and 15%; then the three soil moistures were extracted and analysed together with the tap water. Results show that the difference between the tap water and the extracted soil moisture is within ±2‰ for δ^2H and ±0.2‰ for δ^{18}O.

Limited shallow groundwaters (GG1–GG4 and GG6) with depth ranging from 20 to 30 m and one spring (GG5; Table II) around the soil sampling sites were collected for stable isotopes, tritium and water chemistry measurements. Stable isotopes for groundwater and soil moisture samples were measured at the Laboratory of Water Isotopes and Water-Rock Interaction, Institute of Geology and Geophysics, Chinese Academy of Sciences, by using Picarro L1102-i isotopic water liquid analyser. Results are reported as δ^2H and δ^{18}O ($\delta = (R_{sample} / R_{standard} - 1) \times 1000$) using the Vienna Standard Mean Ocean Water as the standard. The analytical precision is ±0.5‰ for δ^2H and 0.1‰ for δ^{18}O. Tritium was measured in the same laboratory through electrolytic enrichment with a tritium enrichment factor of ~20 and liquid scintillation counting (Quantulus 1220) method with a detection limit of 0.3 TU. Anions were analysed by ion chromatography (Dionex-500) and cations by inductively

Table I. The average moisture content and chloride concentration below 2 m for profiles under different land use from Hequan, Guyuan

Profile	Land use	Depth (m)	Moisture content (%)	Cl content (mg l^{-1})
G1	Natural grassland	14.25	17.3	7.7
G1-2	Natural grassland	7.00	16.2	8.1
G2-1	Winter wheat	11.25	15.2	13.9
G2-2	Winter wheat	18.25	16.4	15.4
G3	Alfalfa	7.00	9.5	89.1

Table II. The water isotopic compositions (^{3}H, ^{2}H and ^{18}O) and water chemistry for groundwater samples from Hequan, Guyuan (locations can be found in Figure 1)

Sample	Depth (m)	^{3}H (TU)	δ^{18}O (‰)	δ^2H (‰)	Cl^- (mg l^{-1})	SO_4^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
GG1	30	<0.3	−9.9	−68.8	8.3	27.1	322	52.1	3.2	24.1	42.0
GG2	20	<0.3	−9.7	−68.6	8.1	22.3	326	50.6	4.6	26.1	42.1
GG3	22	<0.3	−9.8	−69.3	8.4	28.1	366	55.6	2.3	26.2	46.8
GG4	22	<0.3	−9.4	−67.8	7.9	25.7	374	53.7	2.3	28.2	45.1
GG5	—	<0.3	−10.0	−70.1	9.9	33.2	416	85.2	3.0	27.9	37.5
GG6	28	<0.3	−9.6	−69.0	8.1	24.3	328	51.2	2.9	24.5	42.9

coupled plasma optical emission spectrometer at the Beijing Research Institute of Uranium Geology. The analytical precision for water chemistry was 3% of the concentration based on reproducibility of samples and standards, and the detection limit was 0.05 mg l^{-1}. The charge balance error for groundwater samples ranges from −2 to 2%.

RESULTS AND DISCUSSION

Groundwater recharge under initial conditions

Chloride input. There are no systematic observations of chloride deposition in the study area. However, several measurements in other sites in the LPC or close to the LPC can be used. The volume-weighted average chloride concentration in precipitation for a remote monitoring station, Jiwozi, in the vicinity of Xi'an, south part of the LPC (EANET, 2009), is 1.7 mg l^{-1}. The data represent the monthly monitoring data from 2001 to 2007. The value agrees well with the average chloride concentrations of precipitation from 23 precipitation samples (1.7 mg l^{-1}) measured by Xu *et al.* (2009) in Lanzhou and from 34 precipitation samples (1.8 mg l^{-1}) measured by Bai and Wang (2008) in Xi'an from February 2007 to January 2008. In the northern Qilian mountains (Feng *et al.*, 2004), the Badain Jaran Desert (Gates *et al.*, 2008; Ma and Edmunds, 2006), the Tengger Desert (Edmunds *et al.*, 2006; Ma *et al.*, 2009), Shiyang River Basin (Ma *et al.*, 2012) and the southern Qinling mountains (Bu HM, unpublished), the rainfall chloride concentration available mainly ranges from 1.4 to 2.5 mg l^{-1}.

Generally, high chloride concentration corresponds to light rainfall in the North-western China (Yin *et al.*, 2011a; Ma *et al.*, 2012), where more than 60–70% of the annual precipitation falls in the summer monsoon. During the period, the chloride concentration in precipitation mainly ranges from 0.88 to 4 mg l^{-1} in the Ordos Basin (Yin *et al.*, 2010). The weighted average chloride concentration in precipitation is 2.24 mg l^{-1} in the Hailiutu River Basin with precipitation of 380 mm year^{-1} in the Ordos Basin (Yin *et al.*, 2011a). The wet chloride input (Clp × P) ranges from 637 to 983 mg m^{-2} year^{-1} (Yin *et al.*, 2010; Deng *et al.*, 2011) in the Ordos Basin for seven sites except for three where the only occasional chloride value in precipitation cannot be used to present the average value.

In arid area, a part component of chloride input can be also derived from dry deposition and dust (Dettinger, 1989; Abuduwaili *et al.*, 2008). In the Basin and Range Province groundwater recharge study, the average chloride content in bulk precipitation from eight sites is 0.6 mg l^{-1}, whereas the wet precipitation content from 66 sites is 0.4 mg l^{-1} (Dettinger, 1989). This means dry deposition may contribute as much as 33% of the total influx of chloride. In a Douglas-fir site on the western slopes of the Washington Cascades and the Great Smokey Mountain National Park, North Carolina, the dry deposition is 13–18% of the total influx of chloride (Johnson and Lindberg, 1992), and in the Hutuo Basin in the North China Plain, it is estimated to be 10% (Liu *et al.*, 2009). However, because of the errors and uncertainties during the bulk precipitation collecting, samples from bulk precipitation collectors may not represent the net influx of chloride input, and simply collected bulk samples may overestimate atmosphere input of chloride to recharge (Dettinger, 1989). Therefore, recharge estimates presented by Dettinger (1989) were based on the average concentration from wet precipitation concentration (0.4 mg l^{-1}). For low rates of flux, errors introduced by the uncertainty of the effective chloride concentration and/or precipitation may have to be tolerated, as other tracers also suffer uncertainties at low flux (Tyler *et al.*, 1996). Goni *et al.* (2001) also commented that the dry aerosol flux deposition can be negligible, which is acceptable provided that the long-term dry aerosol flux is near a steady state. This is a reasonable assumption in the semiarid LPC. An example can demonstrate the assumption. The excellent tritium peak method shows that groundwater recharge rates in the two loess-covered regions – Wudan in Inner Mongolia (precipitation of 360 mm year^{-1}) and Pingding in Shanxi (precipitation of 550 mm year^{-1}) – are 47 and 68 mm year^{-1}, respectively (Lin and Wei, 2001; Lin and Wei, 2006). The total chloride input to soil can be obtained using the inverse CMB. As the chloride content in soil moisture in the unsaturated zone is 9.3 and 19.5 mg l^{-1}, the total chloride input is 437 and 1326 mg m^{-2} year^{-1}, corresponding to 1.2 and 2.4 mg l^{-1} of chloride content in bulk precipitation (including dry deposition), respectively. The chloride content in bulk precipitation covers the range of chloride content in wet precipitation in the LPC.

The CMB method needs constant rate of chloride deposition to the surface. Although this will certainly vary, it is unlikely to vary greatly for the following reasons (Tyler *et al.*, 1996). (i) As the chloride content in precipitation is most strongly controlled by the proximity to its ocean source, the wet deposition flux should be linearly proportional to the precipitation, assuming that the source of the precipitation has remained constant. This is suitable to the LPC as the climate pattern has not been changed during a short period of chloride accumulation in the unsaturated zone (decades to hundreds of years). (ii) Correlations between major climatic variation and chloride age found by Fouty (1989) and Phillips (1994) support the assumption of consistency in chloride deposition. In addition, the remote station in Jiwozi, as well as in Hequan (the study area), is located in an area with minimum influence of local emission contamination and emission sources (such as residential, power plant, factory, toll road, and harbour and train road sources). The weighted chloride content (1.7 mg l^{-1}) in Jiwozi is very similar to that in the urban sites, e.g. in Lanzhou (1.7 mg l^{-1}) and in Xi'an (1.8 mg l^{-1}). In the North-western China, the intensity of human activities is weaker than that in the south China, and their influences are neglected during the period of recharge estimation in this study.

A value of 1.7 mg l^{-1} is adopted because of the lack of observation in the study area; the annual atmospheric chloride deposition from the atmosphere is thus expected to be 765 mg m^{-2} year^{-1} (450 mm year^{-1} × 1.7 mg l^{-1}) for Guyuan and is within the ranges in the north Ordos Basin (Yin *et al.*, 2010) and in Wudan and Pingding (Lin and Wei, 2001).

Feasibility of the CMB. In this loess material, the geological sources of Cl can be excluded. Feth (1981) commented that where groundwater contains less than 10 mg l^{-1} chloride, atmospheric sources are probably the major source. In the study area, chloride contents in groundwater range from 7.9 to 9.9 mg l^{-1} (Table II). In the type site of LPC, chloride contents in groundwater are commonly less than 10 mg l^{-1} (LPISST, 1990; Huang, 2010). There are no rock salt sources in the unsaturated zone with respect to the present chloride. In well-drained soil, this appears to be a reasonable approximation (Allison and Hughes 1978). The chloride input flux has excluded the chemical fertilizers used in the area, in which there is no detected chloride. The possible manure fertilizer to the cultivated land in the study area is limited within an error of ~5–10% for atmospheric deposition and then is ignored. In a homogeneous unsaturated zone, soil water moves down mainly by piston flow (Zimmermann *et al*., 1967). The loess, including the palaeosol is unconsolidated, and the homogeneous porosity suggests that no significant preferential flow occurs in the loess deposition area, except near the cliffs and the gullies. The obvious 1963 tritium peak in the unsaturated zone in the loess-covered regions (Zhang *et al*., 1990; Lin and Wei, 2006; Baran *et al*., 2007) confirmed the existence of piston flow in loess. The breakthrough curves obtained for chloride, nitrate and tritiated water from six undisturbed columns of loess showed that homogeneous infiltration seems to be a rather intrinsic characteristic of loess (El Etreiby and Laudelout, 1988). In loess-covered areas, the CMB thus has significance as a recharge estimator (O'Brien *et al*., 1996; O'Geen *et al*., 2005; Huang and Pang, 2011; Gates *et al*., 2011).

Rates of recharge. Profile G1-2 is taken as the initial condition of the area. The gravimetric moisture contents of >18% above 0.75–1.00 m show the effects of seasonal rainfall events before sampling. From a depth of 0.75–2.00 m, the moisture contents range from 9.7 to 12.2% (Figure 3). The chloride is concentrated, and moisture is depleted by evapotranspiration and remains in

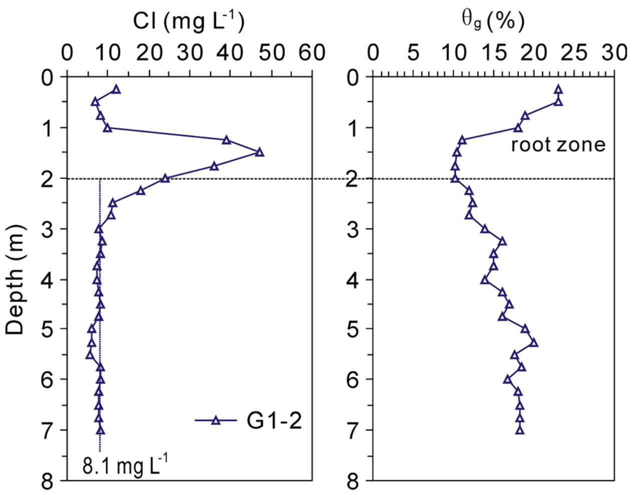

Figure 3. Soil chloride concentration and moisture content profile for G1-2 of natural grassland in Hequan, Guyuan

the root zone until it is flushed downward below the root zone (commonly below 2 m; Allison and Hughes, 1978; Vörösmarty *et al*., 1989) by infiltrating precipitation. Below the root zone, the moisture represents potential recharging pore water with relatively uniform chloride distribution (5.5 to 11.2 mg l^{-1}; Figure 3).

The average weighted chloride concentration below the root zone for G1-2 (natural ecosystem) is 8.1 mg l^{-1} to a depth of 7 m. The groundwater recharge rate beneath the natural ecosystem is 765 / 8.1 = 94 mm year^{-1} by using Equation 1, accounting for 21% of the annual precipitation. The average chloride content in soil moisture below the root zone to 14.25 m for baseline profile G1 (Huang and Pang, 2011) is 7.7 mg l^{-1}, similar to profile G1-2. The similar distributions of chloride and soil moisture content are remarkably convergent and indicate the recharge beneath the natural ecosystem is in the order of 94–100 mm year^{-1}.

This recharge rate beneath the natural ecosystem is 2–3 orders of magnitude more than in the other semiarid areas with similar annual rainfall, e.g. <0.1 mm year^{-1} under mallee in the western Murray Basin (Allison *et al*., 1990), almost zero under shortgrass prairie in the southern High Plains, Texas, south-western USA (Scanlon *et al*., 2007b), <0.33 mm year^{-1} under dry forests in central Argentina (Santoni *et al*., 2010) and 2 mm year^{-1} under natural bush in South-west Niger (Leduc *et al*., 2001; Favreau *et al*., 2009). The large difference of the recharge rate beneath the natural ecosystem is related to different vegetation with different root type (deep or shallow rooted) and temperature (Table III). Compared with other case study areas with an annual mean temperature of 15–30 °C, the LPC is a relatively cold semiarid area with an annual mean temperature of 6–9 °C.

The average chloride concentration in unsaturated zone moisture of 7.7 to 8.1 mg l^{-1} is similar to that in groundwaters, which ranges from 7.9 to 9.9 mg l^{-1} (Table II), indicating that diffuse recharge is likely to be the predominant source of recharge.

Residence time of infiltrating water. The regional groundwater depth ranges from 25 to 100 m (30–120 m is typical for the LPC as a whole; Figure 1). For profiles G1 and G1-2, the average volumetric water content is estimated to be ~24% (gravimetric water content 17% × the soil dry bulk density 1.4). The recharging time beneath the natural ecosystem can be determined by a simple calculation (25–100) m * 0.24 / [(0.094–0.1) m year^{-1}] = 60–255 years. The shallow groundwaters and the spring around the sampling site are all tritium free (Table II), suggesting that the groundwaters were recharged before 1950s and that they are older than 60 years. Tian *et al*. (2007) and Huang (2010) also pointed out that the groundwater ages in many loess plains (e.g. Xifeng, Luochuan, Fuping and Weinan) in the LPC are older than 50 years based on tritium results. This is consistent with the piston flow model and the CMB results, with no evidence of by-pass flow (Edmunds and Walton, 1980). On the condition of deep unsaturated zone (deep water table), the variation of the recharge rate tends to be small, and the annual recharge rate may be treated as

Table III. Groundwater recharge rate under different natural ecosystem and crop in selected semiarid areas

Study area	Natural vegetation	Root type	Precipitation (mm year^{-1})	Annual mean temperature (°C)	Recharge under natural vegetation (mm year^{-1})	Recharge under crops (mm year^{-1})	Reference
Western Murray Basin, Australia	Mallee	Deep	250–450	~20	<0.1	17 (average)	Allison *et al*., 1990
Southern High Plains, the USA	Shortgrass prairie	Deep	376–501	~15	0	24 (median)	Scanlon *et al*., 2007b; 2009
Central Argentina	Dry forests	Deep	350–600	~16	0.02–0.33	6.9–128.4	Santoni *et al*., 2010
South-west Niger	Natural bush	Deep	557	29	2	25 ± 7	Leduc *et al*., 2001; Favreau *et al*., 2009
Xifeng, LPC	Grassland	Shallow	523	8.5	—	33–38	Qu, 1991; Huang and Pang, 2011
Ansai, LPC	Grassland	Shallow	500	8.8	—	55–90	Gates *et al*., 2011
Hequan, LPC	Grassland	Shallow	450	6.6	94–100	50–55	This study

constant (Wu *et al*., 1996). A study on the Luochuan Loess Plain (LPISST, 1990; Qu, 1991) with a water table depth ranging from 30 to 80 m shows that the recharge from precipitation to shallow loess groundwater is continuous. Thus, the unsaturated zone represents well the long-term average rate of recharge, smoothing out short-term climatic events. However, these results suggest that the period of 1–3 years suggested by LPISST (1990) and Yan (1986) required for a water molecule of the precipitation to reach water table seems to be significantly underestimated.

Recharge mechanisms. The stable isotopic composition for soil moisture from profile G1 from the surface to a depth of 9 m is relatively enriched ($\delta^{18}O > -8.5$‰, $\delta^2H > 63$‰), but below 9 m, the isotopic composition is close to or depleted compared with the ranges of the groundwaters (from −10.0 to −9.4‰ for $\delta^{18}O$ and from −70.1 to −67.8‰ for δ^2H; Figure 4). The slope of the regression line for profile G1 is 7.5 ($R^2 = 0.97$), greater than the evaporation slope of commonly 4–6 for open water and even to 2–3 for soil evaporation (Barnes and Allison, 1988), and the regression line is sub-parallel to the global meteoric water line (GMWL; Craig, 1961). This also suggests that a certain amount of the water is removed via evaporation (there is no fractionation for stable isotopes during transpiration). The phenomenon is commonly observed in dry climates (e.g. Tyler *et al*., 1996; Chapman *et al*., 2003; Huang and Pang, 2010) and attributed to similar amounts of evaporation to precipitation from different rainfall events having different isotopic compositions. Under relatively low recharge rates and vertical moisture movement, diffusional redistribution in stable isotopes (Allison, 1988) will attenuate the seasonal or yearly variations in isotopes above the water table (Clark and Fritz, 1997) and indicate that shallow groundwaters closely represent the mean annual recharging precipitation.

In temperate areas, stable isotopes are normally depleted in winter and enriched in summer (Clark and Fritz, 1997). However, in the LPC, the summer rainfall is controlled by the east-Asian monsoon (Wei and Lin, 1994; Araguás-Araguás *et al*., 1998) and has significant characteristics: stable isotopes from precipitation are depleted from July to September (Figure 5). In this setting, the temperature effect is masked by the amount effect.

Stable isotopic compositions for shallow groundwaters from the study area (elevation = 1800–1900 m, a.s.l.), the Ansai terrace (1100–1200 m; Gates *et al*., 2011), the Chibagou hilly region (898–1302 m); (Liu *et al*., 2011) and typical loess plains, e.g. Changwu (~1200 m; Wang, 2007), Xifeng (~1420 m), Luochuan (~1150 m; Huang, 2010) and Xi'an (400–1200 m; Qin and Tao, 2001) are all close to the GMWL and are depleted in heavy isotopes (Figure 6), compared with the weighted average of −6.6‰ for precipitation from Yinchuan (1112 m) in the northern LPC, −7.1‰ from Xi'an (400 m) in the south (IAEA and WMO, 2009) and −7.8‰ in the Ordos Basin (Yang *et al*., 2009). It is difficult to find the traditional 'isotopic altitude and latitude effect' for precipitation (Yang *et al*., 2009) and in groundwater. According to the only basin-scale study in the LPC, an 'altitude effect' for precipitation does not

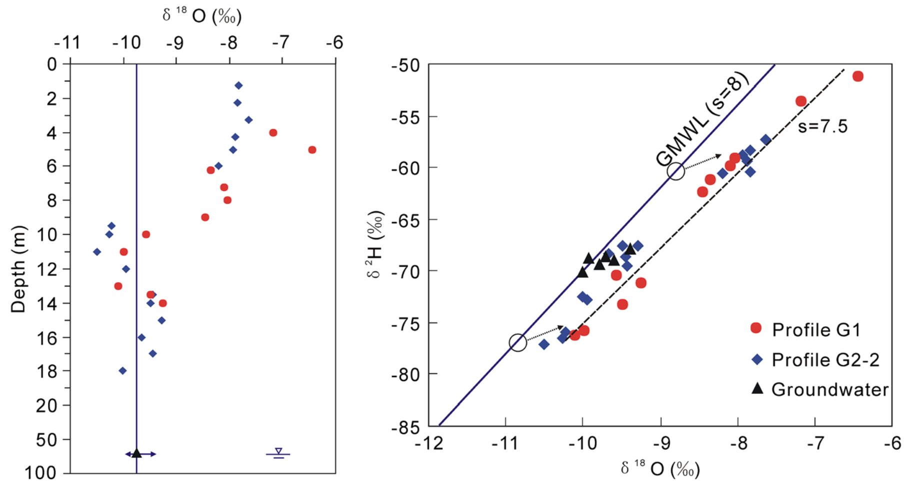

Figure 4. Stable isotopic compositions of soil moisture (G1 and G2-2) and groundwaters from Hequan, Guyuan

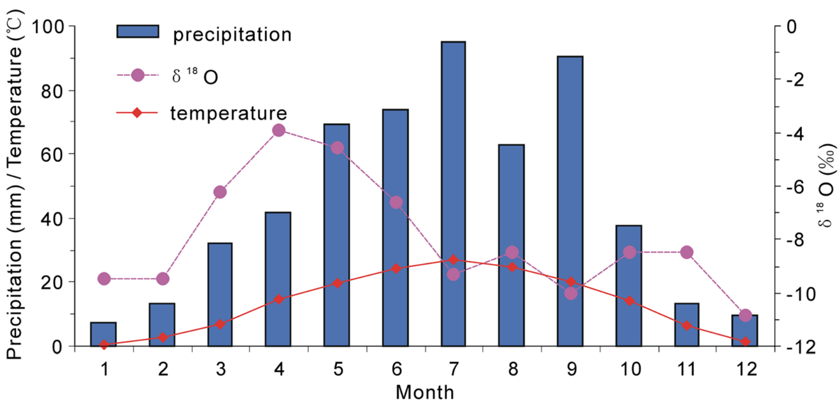

Figure 5. Monthly precipitation, temperature and δ^{18}O composition from Xi'an station [data from IAEA and WMO (2009)]

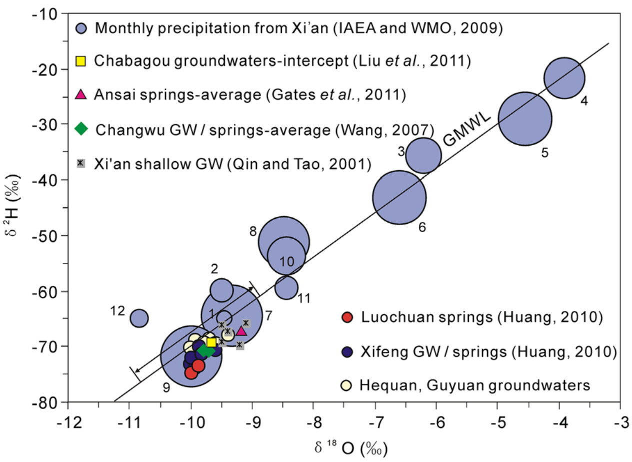

Figure 6. Stable isotopic composition for shallow groundwaters and springs from the LPC [data are from Gates *et al.* (2011) for Ansai, Liu *et al.* (2011) for Chibagou, Wang (2007) for Changwu, Huang (2010) for Xifeng and Luochuan, Qin and Tao (2001) for Xi'an and IAEA and WMO (2009) for precipitation from Xi'an]. The size of the blue circle stands for the relative amount of precipitation. The aforementioned locations can be found in Figure 1

occur during the summer monsoon (Liu *et al.*, 2011). This suggests that in the semiarid LPC, groundwater is recharged by seasonal large rainfall with rapid infiltration and not much evaporation. Depleted in heavy isotopes in groundwater relative to mean precipitation was also found in other arid areas, e.g. southern Africa (Vogel and Urk, 1975) and the southern Great Basin, USA (Tyler *et al.*, 1996), and attributed to selective infiltration of rainfall from intense, large-volume, isotopically light rainfall events. Stable isotopic compositions for groundwaters from the six sites are close to precipitation from July to September in Xi'an (Figure 6), implying that the moisture, which could pass through the root zone and become potential recharge and eventually recharge aquifer, is associated with the monsoon (July to September).

The evidence that (i) Cl concentration in the soil profile (7.7–8.1 mg l^{-1}) is similar to that in groundwaters (7.9–9.9 mg l^{-1}), (ii) stable isotopic composition in groundwaters is limited to the range of that in soil moisture and (iii) groundwater ages of more than 60 years (as obtained from tritium) are consistent with that obtained by piston–CMB method (60–255 years) all suggest that the vertical piston flow is the main mechanism for soil water movement and recharge, at least in this study area.

Changes in groundwater recharge following land-use change

Profiles G2-1 and G2-2 represent a 100-year-old winter wheat field, and profile G3 represents a 30-year-old alfalfa field converted from a winter wheat field. The conversions from G1 (G1-2) to G2-1 (G2-2) and then to G3 provide a long-term land-use change setting through which to study these effects on groundwater recharge.

The only factor affecting groundwater recharge in this small area with the same soil texture (Malan Loess) and topography (flat terrace) is assumed to be evapotranspiration. Chloride concentration profiles monitor the changes in evapotranspiration. Increased chloride concentration implies decreased groundwater recharge (Equation 1) and vice versa.

Moisture content and Cl concentration in the root zone are sensitive to seasonal precipitation and evapotranspiration. For groundwater recharge estimation, depths below 2 m were chosen to study the moisture content and Cl concentration distributions under varying land-use settings. Table I lists the weighted average chloride content and the moisture content and illustrates impacts from the natural ecosystem (G1 and G1-2) to winter wheat (G2-1 and G2-2) and then to alfalfa (G3), where chloride is progressively concentrated. Figure 7 also shows the moisture content and Cl concentration distributions for the five profiles.

Profiles G2-1 and G2-2 beneath winter wheat were converted from a natural ecosystem 100 years ago. The weighted average chloride concentrations below the root zone are 13.9 and 15.4 mg l^{-1} for G2-1 (11.25 m) and G2-2 (18.25 m), respectively, and 7.7 and 8.1 mg l^{-1} for G1 (14.25 m) and G1-2 (7 m), respectively. On the basis of the CMB method, the potential groundwater recharge has decreased from 94–100 to 50–55 mm $year^{-1}$ as a result of this land-use change. The recharge rate beneath winter wheat of 50–55 mm $year^{-1}$ or 11–13% of the mean annual precipitation is similar to ratios reported for other sites in the LPC, e.g. 12 and 13% (using 1963 tritium peak displacement; Lin and Wei, 2006), 11–18% (using the CMB method; Gates, *et al.*, 2011) and 2.9–23% in the Ordos Basin (Yin *et al.*, 2010).

The soil moisture has been significantly depleted and Cl concentrated (89.1 mg l^{-1}) below 2 m beneath the 30-year-old alfalfa (G3). Here, a new steady-state condition has not been reached, and the CMB cannot be used to estimate the potential groundwater recharge; however, it is predicted that the plantation of alfalfa has been preventing deep drainage because the upper soil are heavily depleted in moisture content. Results from soil water balance within the uppermost 1 m (Zhao *et al.*, 2004) show that the net change in soil water is negative in every month of the growing season beneath the alfalfa field. A study on an alfalfa field following yearly sampling (Li and Huang, 2008) also shows soil moisture is being depleted year after year.

The Cl concentration in groundwaters beneath the new land use in Hequan, Guyuan, is similar to that in soil moisture of original natural vegetation (profiles G1 and G1-2); this is because it takes (25–100) m * 0.22 / [(0.05–0.055) m $year^{-1}$] = 100–440 years for the soil moisture beneath winter wheat to reach the water table. Thus, most groundwaters in the area with deep water table have not yet been influenced by the new land use, i.e. winter wheat and alfalfa. Long travel times for soil moisture in the unsaturated zone following the changed land use implies that the impacts of lowered groundwater recharge rates on water table can be lagged in time. The time lag is related to the soil moisture content, the recharge rate and the depth of the unsaturated zone. Similar lag effects between the increase in deep drainage and the increase in aquifer recharge have been reported for Australia by Cook *et al.* (1989; 2001) and Jolly *et al.* (1989).

The stable isotopic compositions of soil moisture between G1 and G2-2 are very similar (Figure 4), despite the groundwater recharge being largely different (100 and 50 mm $year^{-1}$). Kinzelbach (2002) pointed out that the stable isotopes method for estimating groundwater recharge

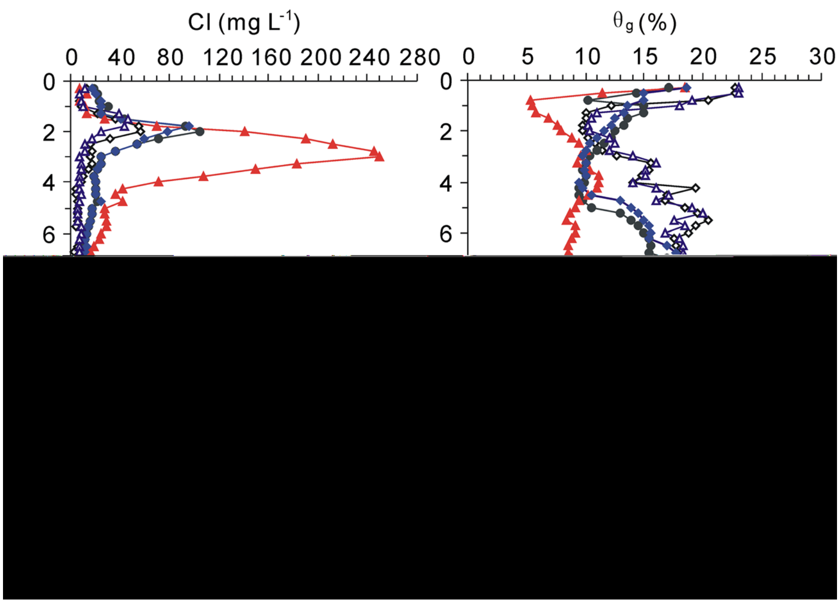

Figure 7. Soil Cl and moisture content distribution under different land uses in Hequan, Guyuan

is not always applicable, because no evaporation signal is seen if recharge happens in extreme events without much evaporation and because evapotranspiration by plants does not produce a shift away from the meteoric water line. An isotopic study in the north LPC (Ansai; Gates *et al*., 2011) shows that stable isotopes in the soil moisture (from cultivated land and shrub plantation) are enriched and follow a low slope ($s = 3.5$), in contrast with shallow groundwater (springs), which showed only slight evaporation pore water (Figure 8a). They suggested that focused infiltration through gullies and other topographic lows is likely to be the primary recharge mechanism in the northern dissected areas. However, in the Xifeng loess plain, where there is no surface runoff and the water table is higher than the gullies, the vertical infiltration of rainfall is the only recharge source (Qu, 1991). A 14.5 m depth stable isotopic profile beneath winter wheat field (~90% land use; Huang, 2010) shows that stable isotopes in the soil moisture are also enriched compared with those in springs (Figure 8b). The average chloride content beneath winter wheat is 27.3 mg l^{-1}, which is higher than that in tritium-free springs (3.1–8.4 mg l^{-1}) in Xifeng (Huang, 2010). The most reasonable explanation based on available data in the situation is that the groundwater was formed under natural baseline land use without much evapotranspiration and that the upper moisture formed in current land use have not reached water table. The stable isotopic profiles therefore cannot be used as a quantitative tool for groundwater recharge estimation but helps to identify groundwater recharge processes and origin.

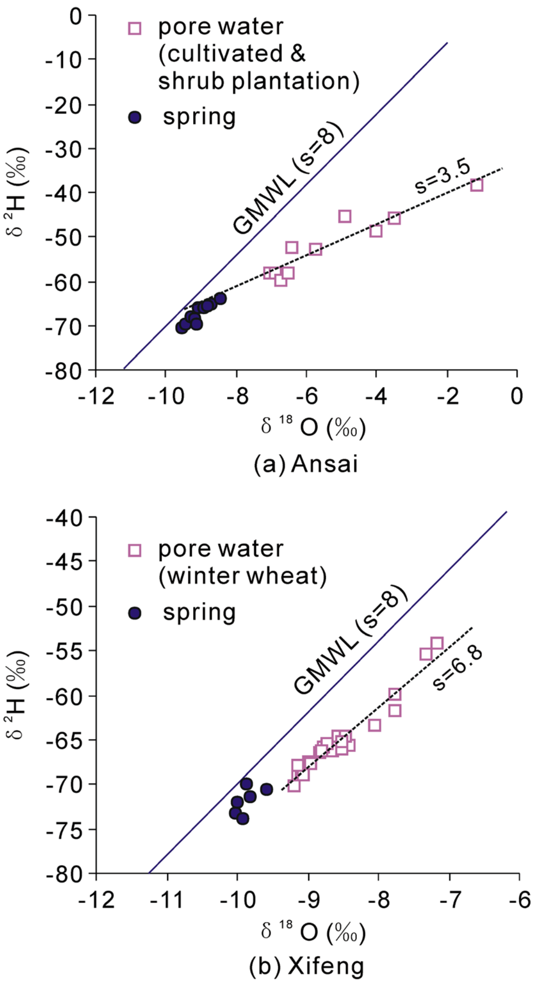

Figure 8. Stable isotopic composition for soil moistures and springs from (a) Ansai and (b) the Xifeng loess plain [modified from Gates *et al*. (2011) and Huang (2010)]

Change in water quality following land-use change

Under circumstances of decreased groundwater recharge following the reported land-use change, the salinity would be expected to increase in the upper unsaturated zone by increased evapotranspiration and then more slowly displace the previous soil water/solutes into groundwater by a decreased drainage rate. Until the moisture with increased solute concentration beneath the changed land use can reach the water table, the former groundwater quality remains.

The soil moisture velocity for profile G2-2 is estimated to be 0.20 m year^{-1} (a depth of 18.25 m and a chloride accumulation age of ~92 years). This is very similar to a tritium peak movement velocity of 0.20–0.21 m year^{-1} for loess areas in France (Baran *et al*., 2007) but a little less than 0.25–0.30 m year^{-1} for the other Chinese loess profiles (Zhang *et al*., 1990; Lin and Wei, 2006). Because the land development started ~100 years ago, below a depth of ~20 m, the moisture and the solutes should remain at the initial land-use setting (natural grassland, e.g. profiles G1 and G1-2). Figure 9 describes the conceptual model of groundwater quality evolution under decreased groundwater recharge based on the present results.

In the study area, the differences in recharge rate and water quality between the natural ecosystem (G1 with a recharge rate of 100 mm year^{-1}) and winter wheat (G2-2 with a recharge rate of 50 mm year^{-1}) may be given as an example of the magnitudes of change. Assuming that the groundwater depth is 25–100 m, the average volumetric water content in the natural ecosystem is 0.24 and 0.22 in winter wheat under both steady states; the time required to reach groundwater beneath winter wheat and to change groundwater quality is 110–440 years. The following parameters may then be used to estimate the groundwater quality evolution for the conversion from natural ecosystem to winter wheat: the chloride concentration of soil moisture entering the aquifer $C_{in} = 15.4$ mg l^{-1}, the new aquifer recharge rate $q = 50$ mm year^{-1}, the initial chloride concentration of shallow groundwater $C_o = 7.7$ mg l^{-1} in the aquifer and the amount of water in the aquifer (porosity, $n = 0.40$; thickness of the aquifer $H = 30$ m). With the use of the assumptions from Equation (2) and the results from Equation (3), we found that after 820 years following land-use conversion, the chloride concentration in groundwater would only reach 15 mg l^{-1} (Figure 10). Thus, the present groundwater quality remains close to the initial land-use setting. The phenomenon of time lag was also found by Peck and Hurle (1973) who showed that the time estimated for chloride equilibrium to be re-established from a forest to a farmland in a small catchment in Australia ranged from 30 to 400 years.

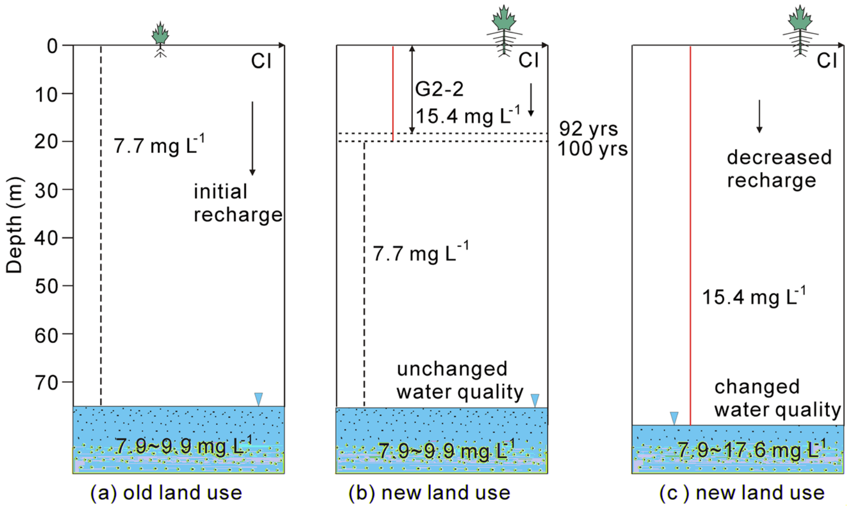

Figure 9. The conceptual model showing groundwater quality evolution under decreased groundwater recharge as a result of increased evapotranspiration following land-use change

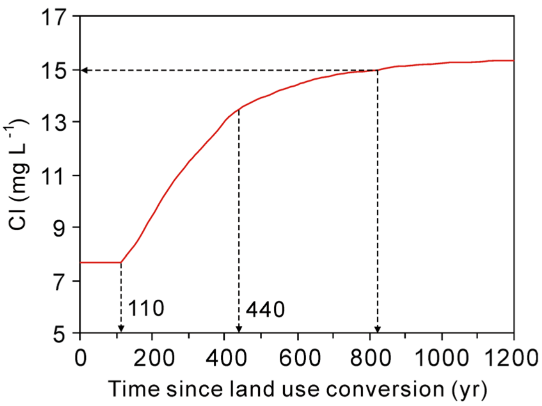

Figure 10. Groundwater quality (chloride concentration) evolution under the conversion from natural grassland to winter wheat in Guyuan

Although the chloride concentration of groundwater would eventually double and total dissolved solids (TDS) be still less than 0.8 g l^{-1}, it should be noticed that the soil moisture containing over-fertilized nitrate and other contaminants would also reach water table and deteriorate groundwater quality. The time lag for groundwater quality change due to buffer of the relatively thick unsaturated zone should be paid attention to for water quality management.

In contrast, plantation of shrubs (Gates *et al.*, 2011), apple orchards (Huang and Pang, 2011) and alfalfa may decrease potential recharge remarkably and lead to higher solute concentration. This compares with very large chloride inventories in dry lands due to high evapotranspiration (e.g. vegetation of shortgrass prairie and eucalyptus mallee) during the predominantly (semi)arid climate of the last 10 000–30 000 years (e.g. Herczeg *et al.*, 2001; Scanlon *et al.*, 2009), even during the last glacial interval (up to 120 000 BP; Tyler *et al.*, 1996). If those land uses (alfalfa, shrub or orchard) change to rain-fed crops (winter wheat) sometime in the future, then increased groundwater recharge would occur, and the groundwater quality would degrade significantly because of the progressive displacement of brackish or saline water, which is happening in the southern USA (Scanlon *et al.*, 2009) and Australia (Leaney *et al.*, 2003) today.

CONCLUSIONS

Groundwater recharge rates and mechanisms in a loess-terrace agriculture region in the semiarid LPC have been examined using multiple tracers, and the impacts of a long-term land-use change on groundwater recharge and water quality have been studied using soil chloride profiles.

1. The groundwater recharge beneath the natural ecosystem (uncultivated shallow-rooted grassland) is 94–100 mm year^{-1} based on the CMB method. It takes decades/hundreds of years for annual precipitation to pass through the thick unsaturated zone, as confirmed by the absence of tritium at the water table. This recharge rate is 2–3 orders of magnitude more than in the other semiarid areas with similar annual rainfall but with deep-rooted vegetation and relatively high temperature.
2. Although stable isotopes cannot be used to measure recharge rates, they can trace the recharge process with information on the water molecules themselves. Groundwater recharge in the study area mainly occurs from July to September almost exclusively by means of vertical infiltration.
3. Comparison of soil chloride profiles before and after land-use change is a useful tool to measure impacts on groundwater resources, especially in (semi)arid areas such as the LPC.
4. The case study of a loess-terrace agriculture region in the LPC shows that the conversion from natural ecosystem to winter wheat 100 years ago has decreased groundwater recharge by 42–50% and that the conversion from winter wheat to alfalfa has decreased to almost zero, consistent with moisture monitoring made by Zhao *et al.* (2004) and Li and Huang (2008).

5. In the circumstances of decreased groundwater recharge following land-use change, solutes would firstly build up at the upper unsaturated zone and then be displaced into groundwater with a decreased drainage rate. There is a time lag between the increase in solute concentration in soil moisture and that in groundwater. Groundwater quality would change when and if the soil water/solutes following the new land use reach water table.
6. The new steady state would nevertheless lead to lowered recharge rates, which need to be taken into account in considering the availability of the regional groundwater resources.

ACKNOWLEDGEMENTS

The work is supported by the National Natural Science Foundation of China (grant no. 40872162) and the China Postdoctoral Science Foundation (grant no. 20110490581). We thank Prof. J.Z. Ma and Dr. J.B. Gates who have contributed to some ideas presented in this manuscript through discussions. We also thank Dr. B. Xu for tritium measurement, Y. M. Li for part of the water chemistry analyses, Z. G. Jin for stable isotope analyses and Y. L. Kong for field work. The authors wish to express their appreciation to three anonymous reviewers whose detailed comments were very helpful in improving the clarity and focus of the manuscript.

REFERENCES

Abuduwaili J, Gabchenko MV, Xu J. 2008. Eolian transport of salts-A case study in the area of Lake Ebinur (Xinjiang, Northwest China). *Journal of Arid Environments* **72**: 1843–1852. DOI: 10.1016/j.jaridenv.2008.05.006.

Allison GB, Cook PG, Barnett SR, Walker GR, Jolly ID, Hughes MW. 1990. Land clearance and river salinisation in the western Murray Basin, Australia. *Journal of Hydrology* **119**: 1–20. DOI: 10.1016/0022-1694(90)90030-2.

Allison GB, Gee GW, Tyler SW. 1994. Vadose-zone techniques for estimating groundwater recharge in arid and semiarid regions. *Soil Science Society of America Journal* **58**: 6–14. DOI: 10.2136/sssaj1994.03615995005800010002x.

Allison GB, Hughes MW. 1978. The use of environmental chloride and tritium to estimate total recharge to an unconfined aquifer. *Australian Journal of Soil Research* **16**: 181–195. DOI: 10.1071/SR9780181.

Allison GB. 1988. A review of some of the physical, chemical and isotopic techniques available for estimating groundwater recharge. In *Estimation of Natural Groundwater Recharge*, Simmers I (ed). Reidel: Dordrecht; 49–92.

Appelo CAJ, Postma D. 1993. *Geochemistry, Groundwater and Pollution*. A. A. Balkema: Rotterdam; 536.

Araguás-Araguás L, Froehlich K, Rozanski K. 1998. Stable isotope composition of precipitation over Southeast Asia. *Journal of Geophysical Research* **103**(D22): 28721–28742. DOI: 10.1029/98JD02582.

Bai L, Wang ZL. 2008. Chemical composition and potential sources of major ions in precipitation in the Xi'an district, Shaanxi province. *Earth and Environment* **36**(4): 289–296 (in Chinese with English abstract).

Baran N, Richert J, Mouvet C. 2007. Field data and modelling of water and nitrate movement through deep unsaturated loess. *Journal of Hydrology* **345**: 27–37. DOI: 10.1016/j.jhydrol.2007.07.006.

Barnes CJ, Allison GB. 1988. Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. *Journal of Hydrology* **100**: 143–176. DOI: 10.1016/0022-1694(88)90184-9.

Böhlke JK. 2002. Groundwater recharge and agricultural contamination. *Hydrogeology Journal* **10**: 153–179. DOI: 10.1007/s10040-002-0210-z.

Calder IR. 1998. Water use by forests, limits and controls. *Tree Physiology* **18**: 625–631. DOI: 10.1093/treephys/18.8-9.625.

Chapman JB, Lewis B, Greg L. 2003. Chemical and isotopic evaluation of water sources to the fens of South Park, Colorado. *Environmental Geology* **43**: 533–545. DOI: 10.1007/s00254-002-0678-9.

Chen HS, Shao MA, Li YY. 2008. Soil desiccation in the Loess Plateau of China. *Geoderma* **143**: 91–100. DOI: 10.1016/j.geoderma.2007.10.013.

Chen JS, Liu XY, Wang CY, Rao WB, Tan HB, Dong HZ, Sun XX, Wang YS, Su ZG. 2011. Isotopic constraints on the origin of groundwater in the Ordos Basin of northern China. *Environmental Earth Sciences*. DOI: 10.1007/s12665-011-1259-6.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology*. Lewis: Boca Raton; 328.

Cook PG, Leaney FW, Miles M. 2004. *Groundwater recharge in the north-east mallee region, South Australia*. CSIRO Publishing: Adelaide; 80.

Cook PG., Hughes MW, Walker GR, Allison GB. 1989. The calibration of frequency-domain electromagnetic induction meters and their possible use in recharge studies. *Journal of Hydrology* **107**: 251–265. DOI: 10.1016/0022-1694(89)90060-7.

Cook PG., Leaney FW, Jolly ID. 2001. *Groundwater recharge in the mallee region and salinity implications for the Murray River*. CSIRO Publishing: Collingwood; 133.

Craig H. 1961. Isotopic variations in meteoric waters. *Science* **133**: 1702–1703. DOI: 10.1126/science.133.3465.1702.

DeFries R, Eshleman KN. 2004. Land-use change and hydrologic processes: a major focus for the future. *Hydrological Processes* **18**: 2183–2186. DOI: 10.1002/hyp.5584.

Deng L, Wang WK, Hu AY. 2011. Estimation of groundwater recharge by chloride mass balance (CMB) method in a typical semiarid climate of China. In *Proceedings of 2011 International Symposium on Water Resources and Environmental Protection*, Xi'an, China. May 2011. IEEE Press; 400–403. DOI: 10.1109/ISWREP.2011.5893029.

Dettinger MD. 1989. Reconnaissance estimates of natural recharge to desert basins in Nevada, USA, by using chloride-balance calculations. *Journal of Hydrology* **106**: 55–78. DOI: 10.1016/0022-1694(89)90166-2.

EANET-Acid Deposition Monitoring Network in East Asia. 2009. EANET data on the acid deposition in the East Asian region. http://www.eanet.cc, [Accessed Dec 2009].

Edmunds WM, Darling WG, Kinniburgh DG. 1988. Solute profile techniques for recharge estimation in semi-arid and arid terrain. In *Estimation of Natural Groundwater Recharge*, Simmers I (ed). Reidel: Dordrecht; 139–157.

Edmunds WM, Ma JZ, Aeschbach-Hertig W, Kipfer R, Darbyshire DPF. 2006. Groundwater recharge history and hydrogeochemical evolution in the Minqin Basin, North West China. *Applied Geochemistry* **21**: 2148–2170. DOI: 10.1016/j.apgeochem.2006.07.016.

Edmunds WM, Walton NRG. 1980. A geochemical and isotopic approach to recharge evaluation in semi arid zones - past and present. In *Arid-zone Hydrology: Investigations with Isotope Techniques*, Fontes JC (ed.). Proceeding of Advisory Group Meeting: Vienna; 47–68.

Edmunds WM. 2010. Conceptual models for recharge sequences in arid and semi-arid regions using isotopic and geochemical methods. In *Groundwater Modelling in Arid and Semi-arid Areas*, Wheater HS, Mathias SA, Li X (eds). Cambridge University Press: Cambridge; 21–37.

El Etreiby F, Laudelout H. 1988. Movement of nitrite through a loess soil. *Journal of Hydrology* **97**: 213–224. DOI: 10.1016/0022-1694(88)90116-3.

Favreau G, Cappelaere B, Massuel S, Leblanc M, Boucher M, Boulain N, Leduc C. 2009. Land clearing, climate variability, and water resources increase in semiarid Southwest Niger: a review. *Water Resources Research* **45**, W00A16. DOI: 10.1029/2007WR006785.

Favreau G, Leduc C, Marlin C, Dray M, Taupin JD, Massault M, Le Gal La Salle C, Babic M. 2002. Estimate of recharge of a rising water table in semiarid Niger from ^{3}H and ^{14}C modeling. *Ground Water* **40**: 144–151. DOI: 10.1111/j.1745-6584.2002.tb02499.x.

Feng Q, Liu W, Su YH, Zhang YW, Si JH. 2004. Distribution and evolution of water chemistry in Heihe River Basin. *Environmental Geology* **45**: 947–956. DOI: 10.1007/s00254-003-0950-7.

Feth JH. 1981. Chloride in natural continental water: a review. US Geological Survey, Water Supply Paper 2176; 30.

Fouty SC. 1989. Chloride mass balance as a method for determining long-term ground-water recharge rates and geomorphic surface stability in arid and semiarid regions: Whiskey Flat and Beatty, Nevada. Master thesis, University of Arizona, Tucson.

Gates JB, Edmunds WM, Ma JZ, Scanlon BR. 2008. Estimating groundwater recharge in a cold desert environment in northern China using chloride. *Hydrogeology Journal* **16**: 893–910. DOI: 10.1007/s10040-007-0264-z.

Gates JB, Scanlon BR, Mu X, Zhang L. 2011. Impacts of soil conservation on groundwater recharge in the semi-arid Loess Plateau, China. *Hydrogeology Journal* **19**: 865–875. DOI: 10.1007/s10040-011-0716-3.

Gaye CB, Edmunds WM. 1996. Groundwater recharge estimation using chloride, stable isotopes and tritium profiles in the sands of northwestern Senegal. *Environmental Geology* **27**: 246–251. DOI: 10.1007/BF00770438.

Gee GW, Hillel D. 1988. Groundwater recharge in arid regions: review and critique of estimation methods. *Hydrological Processes* **2**: 255–266. DOI: 10.1002/hyp.3360020306.

Gee GW, Zhang ZF, Tyler SW, Albright WH, Singleton MJ. 2005. Chloride mass balance: cautions in predicting increased recharge rates. *Vadose Zone Journal* **4**: 72–78.

Ginn TR, Murphy EM. 1997. A transient flux model for convection infiltration: forward and inverse solution for chloride mass balance studies. *Water Resources Research* **33**: 2065–2079. DOI: 10.1029/97WR01618.

Goni IB, Fellman E, Edmunds WM. 2001. Rainfall geochemistry in the Sahel region of northern Nigeria. *Atmospheric Environment* **35**: 4331–4339. DOI: 10.1016/S1352-2310(01)00099-1.

Healy RW, Cook PG. 2002. Using groundwater levels to estimate recharge. *Hydrogeology Journal* **10**: 91–109. DOI: 10.1007/s10040-001-0178-0.

Herczeg AL, Dogramaci SS, Leaney FW. 2001. Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. *Marine and Freshwater Research* **52**: 41–52. DOI: 10.1071/MF00040.

Huang MB, Zhang L. 2004. Hydrological responses to conservation practices in a catchment of the Loess Plateau, China. *Hydrological Processes* **18**: 1885–1898. DOI: 10.1002/hyp.1454.

Huang TM, Pang ZH. 2010. Changes in groundwater induced by water diversion in the Lower Tarim River, Xinjiang Uygur, NW China: evidence from environmental isotopes and water chemistry. *Journal of Hydrology* **387**: 188–201. DOI: 10.1016/j.jhydrol.2010.04.007.

Huang TM, Pang ZH. 2011. Estimating groundwater recharge following land-use change using chloride mass balance of soil profiles: a case study at Guyuan and Xifeng in the Loess Plateau of China. *Hydrogeology Journal* **19**: 177–186. DOI: 10.1007/s10040-010-0643-8.

Huang TM. 2010. Study on groundwater recharge in typical loess-plains in the Loess Plateau of China. Doctoral thesis, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing (in Chinese).

IAEA and WMO. 2009. Water Isotope system for data analysis, visualization, and electronic retrieval (WISER). http://nds121.iaea.org/wiser/ [Accessed Dec 2009]

Jobbágy EG, Jackson RB. 2004. Groundwater use and salinization with grassland afforestation. *Global Change Biology* **10**: 1299–1312. DOI: 10.1111/j.1365-2486.2004.00806.x.

Johnson DW, Lindberg SE. 1992. *Atmospheric Deposition and Forest Nutrient Cycling: A Synthesis of the Integrated Forest Study*. Springer-Verlag: New York; 707.

Jolly I D, Cook PG, Allison GB, Hughes MW. 1989. Simultaneous water and solute movement through an unsaturated soil following an increase in recharge. *Journal of Hydrology* **111**: 391–396. DOI: 10.1016/0022-1694(89)90270-9.

Kinzelbach W. 2002. The Most Common Methods of Recharge Estimation. In *A Survey of Methods for Groundwater Recharge in Arid and Semi-arid Regions*. Early Warning and Assessment Report Series, UNEP/DEWA/RS.02-2, United Nations Environment Programme, Kinzelbach W (ed). ISBN 92-80702131-3. 7–19.

Klein Goldewijk K. 2001. Estimating global land use change over the past 300 years: the HYDE database. *Global Biogeochemical Cycles* **15**: 417–433. DOI: 10.1029/1999GB001232.

Lambin EF, Baulies X, Bockstael NE, Fischer G, Krug T, Leemans R, Moran EF, Rindfuss R, Sato Y, Skole DL, Turner II BL, Vogel C. 2002. Land-use and land-cover change implementation strategy. IGBP Report No. 48 and IHDP Report No. 10, Louvainla-Neuve, Belgium.

Leaney FW, Herczeg AL, Walker GR. 2003. Salinization of a fresh palaeo-ground water resource by enhanced recharge. *Ground Water* **41**: 84–92. DOI: 10.1111/j.1745-6584.2003.tb02571.x.

Leduc C, Favreau G, Schroeter P. 2001. Long-term rise in a Sahelian water-table: the Continental Terminal in South-West Niger. *Journal of Hydrology* **243**: 43–54. DOI: 10.1016/S0022-1694(00)00403-0.

Li XQ, An ZS, Zhou J, Gao HJ, Zhao HL. 2003. Characteristics of vegetation in the Loess Plateau area since Holocene. *Marine Geology & Quaternary Geology* **23**(3): 109–114 (in Chinese with English abstract).

Li YS, Huang MB. 2008. Pasture yield and soil water depletion of continuous growing alfalfa in the Loess Plateau of China. *Agriculture, Ecosystems & Environment* **124**: 24–32. DOI: 10.1016/j.agee.2007.08.007.

Lin RF, Wei KQ. 2001. Environmental isotope profiles of the soil water in loess unsaturated zone in semi-arid areas of China. In *Isotope Based Assessment of Groundwater Renewal in Water Scarce Regions*, Yurtsever Y (ed). IAEA: Vienna; 101–118.

Lin RF, Wei KQ. 2006. Tritium profiles of pore water in the Chinese loess unsaturated zone: implications for estimation of groundwater recharge. *Journal of Hydrology* **328**: 192–199. DOI: 10.1016/j.jhydrol.2005.12.010.

Liu J, Chen ZY, Zhang ZJ, Fei YH, Zhang FE, Chen JS, Wang Z. 2009. Estimation of natural groundwater recharge in the Hutuo River alluvial-proluvial fan using environmental tracers. *Geological Science and Technology Information* **28**(6): 114–118 (in Chinese with English abstract).

Liu TS. 1985. *Loess and the Environment*. Science Press: Beijing; 481 (in Chinese).

Liu X, Song XF, Zhang YH, Xia J, Zhang XC, Yu JJ, Long D, Li FD, Zhang B. 2011. Spatio-temporal variations of δ^2H and δ^{18}O in precipitation and shallow groundwater in the hilly loess region of the Loess Plateau, China. *Environmental Earth Sciences* **63**: 1105–1118. DOI: 10.1007/s12665-010-0785-y.

LPISST-Loessical Plateau Integrated Scientific Survey Team. 1990. *Study on Rational Development and Utilization of Groundwater Resources in Loess Plateau Area*. Xueyuan Publishing House: Beijing; 93 (in Chinese).

Ma JZ, Ding ZY, Edmunds WM, Gates JB, Huang TM. 2009. Limits to recharge of groundwater from Tibetan plateau to the Gobi desert, implications for water management in the mountain front. *Journal of Hydrology* **364**: 128–141. DOI: 10.1016/j.jhydrol.2008.10.010.

Ma JZ, Edmunds WM. 2006. Groundwater and lake evolution in the Badain Jaran Desert ecosystem, Inner Mongolia. *Hydrogeology Journal* **14**: 1231–1243. DOI: 10.1007/s10040-006-0045-0.

Ma JZ, Zhang P, Zhu GF, Wang YQ, Edmunds WM, Ding ZY, He JH. 2012. The composition and distribution of chemicals and isotopes in precipitation in the Shiyang river system, northwestern China. *Journal of Hydrology*. DOI: 10.1016/j.jhydrol.2012.02.046.

Meybeck M, Vörösmarty CJ. 2004. The integrity of river and drainage basin systems: Challenges from environmental change. In *Vegetation, Water, Humans and the Climate: A New Perspective on an Interactive System*, Kabat P. *et al*. (eds). Springer-Verlag: New York; 297–479.

Mu XM, Zhang L, McVicar TR, Chille B, Gau P. 2007. Analysis of the impact of conservation measures on stream flow regime in catchments of the Loess Plateau, China. *Hydrological Processes* **21**: 2124–2134. DOI: 10.1002/hyp.6391.

O'Brien R, Keller CK, Smith JL. 1996. Multiple tracers of shallow ground-water flow and recharge in hilly loess. *Ground Water* **34**: 675–682. DOI: 10.1111/j.1745-6584.1996.tb02055.x.

O'Geen AT, McDaniel PA, Boll J, Keller CK. 2005. Paleosols as deep regolith: implications for ground-water recharge across a loessial climosequence. *Geoderma* **126**: 85–99. DOI: 10.1016/j.geoderma.2004.11.008.

Peck AJ, Hurle DH. 1973. Chloride balance of some farmed and forested catchments in southwestern Australia. *Water Resources Research* **9**: 648–657. DOI: 10.1029/WR009i003p00648.

Phillips FM, Mattick JL, Duval TA. 1988. Chlorine 36 and tritium from nuclear weapons fallout as tracers for long-term liquid movement in desert soils. *Water Resources Research* **24**: 1877–1891. DOI: 10.1029/WR024i011p01877.

Phillips FM. 1994. Environmental tracers for water movement in desert soils of the American southwest. *Soil Science Society of America Journal* **58**: 15–24.

Qin DJ, Tao SH. 2001. Isotope constraints on the hydraulic relationship of ground-waters between quaternary and tertiary aquifer in Xi'an area, Shaanxi province. *Science China Series E* **44**(S1): 72–79. DOI: 10.1007/BF02916792.

Qu HL. 1991. *Assessment of Groundwater Resources in the Arid and Semiarid Land of China*. Science Press: Beijing; 457 (in Chinese).

Revesz K, Woods PH. 1990. A method to extract soil water for stable isotope analysis. *Journal of Hydrology* **115**: 397–406. DOI: 10.1016/0022-1694(90)90217-L.

Santoni CS, Jobbágy EG, Contreras S. 2010. Vadose zone transport in dry forests of central Argentina: role of land use. *Water Resources Research* **46**: W10541. DOI: 10.1029/2009WR008784.

Scanlon BR, Jolly I, Sophocleous M, Zhang L. 2007a. Global impacts of conversions from natural to agricultural ecosystems on water resources: quantity versus quality. *Water Resources Research* **43**: W03437. DOI: 10.1029/2006WR005486.

Scanlon BR, Keese KE, Flint AL, Flint LE, Gaye CB, Edmunds WM, Simmers I. 2006. Global synthesis of groundwater recharge in semiarid and arid regions. *Hydrological Processes* **20**: 3335–3370. DOI: 10.1002/hyp.6335.

Scanlon BR, Reedy RC, Gates JB. 2010. Effects of irrigated agroecosystems: 1. Quantity of soil water and groundwater in the southern High Plains, Texas. *Water Resources Research* **46**: W09537. DOI: 10.1029/2009WR008427.

Scanlon BR, Reedy RC, Stonestrom DA, Prudic DE, Dennehy KF. 2005. Impact of land use and land cover change on groundwater recharge and quality in the southwestern USA. *Global Change Biology* **11**: 1577–1593. DOI: 10.1111/j.1365-2486.2005.01026.x.

Scanlon BR, Reedy RC, Tachovsky JA. 2007b. Semiarid unsaturated zone chloride profiles: archives of past land use change impacts on water resources in the southern High Plains, United States. *Water Resources Research* **43**, W06423. DOI: 10.1029/2006WR005769.

Scanlon BR, Stonestrom DA, Reedy RC, Leaney FW, Gates J, Cresswell RG. 2009. Inventories and mobilization of unsaturated zone sulfate, fluoride and chloride related to land use change in semiarid regions, southwestern United States and Australia. *Water Resources Research* **45**: W00A18. DOI: 10.1029/2008WR006963.

Shi H, Shao MA. 2000. Soil and water loss from the Loess Plateau in China. *Journal of Arid Environments* **45**: 9–20. DOI: 10.1006/jare.1999.0618.

Silburn DM, Cowie BA, Thornton CM. 2009. The Brigalow Catchment Study revisited: effects of land development on deep drainage determined from non-steady chloride profiles. *Journal of Hydrology* **373**: 487–498. DOI: 10.1016/j.jhydrol.2009.05.012.

Smith DB, Wearn PL, Richards HJ, Rowe PC. 1970. Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. In *Proceedings of the Symposium on Isotope Hydrology*, IAEA: Vienna. 73–87.

Stonestrom DA, Scanlon BR, Zhang L. 2009. Introduction to special section on Impacts of Land Use Change on Water Resources. *Water Resources Research* **45**: W00A00. DOI: 10.1029/2009WR007937.

Tian H, Wang WK, Cao YQ, Wang Z, Wang J. 2007. Tritium age calculation of groundwater in Guanzhong Basin. *Journal of Xi'an University of Science & Technology* **27**(3): 382–385 (in Chinese with English abstract).

Tyler SW, Chapman JB, Conrad SH, Hammermeister DP, Blout DO, Miller JJ, Sully MJ, Ginanni JM. 1996. Soil-water flux in the southern Great Basin, United States: temporal and spatial variations over the last 120,000 years. *Water Resources Research* **32**: 1481–1499. DOI: 10.1029/96WR00564.

Vogel JC, Urk HV. 1975. Isotopic composition of groundwater in semi-arid regions of southern Africa. *Journal of Hydrology* **25**: 23–36. DOI: 10.1016/0022-1694(75)90036-0.

Vörösmarty CJ, Moore III B, Grace AL, Gildea MP, Melillo JM, Peterson BJ, Rastetter EB, Steudler PA. 1989. Continental scale models of water balance and fluvial transport: an application to South America. *Global Biogeochemical Cycles* **3**(3): 241–265. DOI: 10.1029/GB003i003p00241.

Wada Y, van Beek LPH, van Kempen CM, Reckman JWTM, Vasak S, Bierkens MFP. 2010. Global depletion of groundwater resources. *Geophysical Research Letters* **37**: L20402. DOI: 10.1029/2010GL044571.

Walker GR, Jolly ID, Cook PG. 1991. A new chloride leaching approach to the estimation of diffuse recharge following a change in land use. *Journal of Hydrology* **128**: 49–67. DOI: 10.1016/0022-1694(91)90131-z.

Wang R. 2007. Study on interaction among precipitation, soil water and groundwater in a loess-plain based on environmental isotopes. Doctoral thesis, Institute of Soil and Water Conservation, Chinese Academy of Sciences and Ministry of Water Resources, Xi'an (in Chinese).

Wattenbach M, Zebisch M, Hattermann F, Gottschalk P, Goemann H, Kreins P, Badeck F, Lasch P, Suckow F, Wechsung F. 2007. Hydrological impact assessment of afforestation and change in tree-species composition – a regional case study for the Federal State of Brandenburg (Germany). *Journal of Hydrology* **346**: 1–17. DOI: 10.1016/j.jhydrol.2007.08.005.

Wei KQ, Lin RF. 1994. The influence of the monsoon climate on the isotopic composition of precipitation in China. *Geochimica* **23**(1): 33–41 (in Chinese with English abstract).

Wu J, Zhang R, Yang J. 1996. Analysis of rainfall-recharge relationships. *Journal of Hydrology* **177**: 143–160. DOI: 10.1016/0022-1694(95)02935-4.

Xu ZF, Li YS, Tang Y, Han GL. 2009. Chemical and strontium isotope characterization of rainwater at an urban site in Loess Plateau, Northwest China. *Atmospheric Research* **94**: 481–490. DOI: 10.1016/j.atmosres.2009.07.005.

Yan TB. 1986. Discussion on recharge time of shallow groundwater in the Loess Plain of China. *Hydrogeology & Engineering Geology* **25**(3): 42–44 (in Chinese).

Yang WZ, Yu CZ. 1992. *Regional control and evaluation in the Loess Plateau of China*. Science Press: Beijing; 424 (in Chinese).

Yang YC, Shen ZL, Weng DG, Hou GC, Zhao ZH, Wang D, Pang ZH. 2009. Oxygen and hydrogen isotopes of waters in the Ordos Basin, China: implications for recharge of groundwater in the north of cretaceous groundwater basin. *Acta Geologica Sinica-English Edition* **83**: 103–113. DOI: 10.1111/j.1755-6724.2009.00012.x.

Yin LH, Hou GC, Huang JT, Li Y, Wang XY, Yang Z, Zhou YX. 2011a. Using chloride mass-balance and stream hydrographs to estimate groundwater recharge in the Hailiutu River Basin, NW China. In *Proceedings of 2011 International Symposium on Water Resources and Environmental Protection*, Xi'an, China. May 2011. IEEE Press; 325–328. DOI: 10.1109/ISWREP.2011.5893010.

Yin LH, Hou GC, Tao ZP, Li Y. 2010. Origin and recharge estimates of groundwater in the Ordos Plateau, People's Republic of China. *Environmental Earth Sciences* **60**: 1731–1738. DOI: 10.1007/s12665-009-0310-3.

Yin LH, Hu GC, Huang JT, Wen DG, Dong JQ, Wang XY, Li HB. 2011b. Groundwater-recharge estimation in the Ordos Plateau, China: comparison of methods. *Hydrogeology Journal* **19**: 1563–1575. DOI: 10.1007/s10040-011-0777-3.

Zhang H, Hiscock KM. 2010. Modelling the impact of forest cover on groundwater resources: a case study of the Sherwood Sandstone aquifer in the East Midlands, UK. *Journal of Hydrology* **392**: 136–149. DOI: 10.1016/j.jhydrol.2010.08.002.

Zhang L, Dawes WR, Walker GR. 2001. Response of mean annual evapotranspiration to vegetation changes at catchment scale. *Water Resources Research* **37**: 701–708. DOI: 10.1029/2000WR900325.

Zhang X, Zhang L, Zhao J, Rustomji P, Hairsine P. 2008. Responses of streamflow to changes in climate and land use/cover in the Loess Plateau, China. *Water Resources Research* **44**, W00A07. DOI: 10.1029/2007WR006711.

Zhang ZG, Liu FZ, Zhang HP, Liu EK. 1990. Study of soil water movement and recharge rate of rainfall infiltration in aeration zone of loess by measuring natural tritium. *Hydrogeology & Engineering Geology* **29**(3): 5–7 (in Chinese with English abstract).

Zhao C, Feng Z, Chen G. 2004. Soil water balance simulation of alfalfa (*Medicago sativa L.*) in the semiarid Chinese Loess Plateau. *Agricultural Water Management* **69**: 101–114. DOI: 10.1016/j.agwat.2004.04.006.

Zimmermann U, Munnich KO, Roether W. 1967. Downward movement of soil moisture traced by means of hydrogen isotopes. In *Isotope Techniques in the Hydrologic Cycle*, Geophysical Monograph Series 11, American Geophysical Union. 28–36. DOI: 10.1029/GM011p0028.

