

# Spatio-temporal variations of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation and shallow groundwater in the Hilly Loess Region of the Loess Plateau, China

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**Abstract** Groundwater is of utmost significance to socio-economic development and ecological recovery for the Loess Plateau. However, studies regarding the mechanism governing groundwater recharge over this area appear to be inadequate. This study is to examine the spatio-temporal variations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in precipitation and shallow

groundwater. On the basis of this, the mechanisms governing shallow groundwater recharge were explored. Precipitation and groundwater were sampled monthly from May to October during the period 2004–2006 at 13 sites in the Chabagou Catchment (187 km<sup>2</sup>). In the Caopingxigou Experimental Watershed (0.1 km<sup>2</sup>), meteorological variables were observed and rainfall larger than 5 mm was sampled immediately after each rain event. Across the area, 90% of the precipitation occurred from May to September primarily in the form of heavy rains or rainstorms with great spatial variability. There were about 30 localized rains in each year. It was indicated that there existed notable seasonality and pronounced spatial variability in precipitation isotopic compositions. Contributing factors and indications of isotopic compositions, as well as their climatic indications such as monsoon intensities and mixing processes of water vapor, were investigated. The  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  relation of groundwater was found to be  $\delta^2\text{H} = 3.22 \times \delta^{18}\text{O} - 38.1$ , deviating from the local meteoric water line  $\delta^2\text{H} = 7.57 \times \delta^{18}\text{O} + 3.9$ . The range of  $\delta$  values in groundwater is shrunken to be 15–21% of that in individual precipitations, and groundwater in the middle reaches shows a wider range of  $\delta$  values. Isotopic results showed that groundwater originates from precipitation with hydrogen and oxygen isotopic compositions being  $-69$  and  $-9.7\text{‰}$ , respectively, and most groundwater experiences serious evaporation and adequate mixing with old water during infiltration or percolation in the aerated zone. It was also founded that obvious fluctuations of isotopic compositions in groundwater mainly appear in the middle reaches especially at sites that are close to valleys, suggesting varying sources of groundwater from precipitation, precipitation runoff, isotopically enriched surface water and/or lateral recharge of adjacent groundwater.

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## Introduction

Groundwater is of great significance to agriculture, domestic use, industrial production, environmental construction and ecological restoration over the semi-arid Hilly Loess Region of the Loess Plateau, Northwest of China. Studying the mechanisms governing groundwater recharge plays a vital role in properly utilizing local groundwater resources and in effectively mitigating eco-environmental problems over these areas. Initiated by serious soil and water losses in the Loess Plateau, present studies primarily focus on land surface processes, i.e., precipitation distribution (Zhang 1983; Lin and Wang 2007), land cover change (Xin et al. 2008), runoff generation processes (Li and Shao 2004; Xia et al. 2007), soil water dynamics (Li and Huang 2008), relationships between runoff and sediment (Xu 1998; Fang et al. 2007), and hydrologic effects of soil and water conservation measures (Liu and Zhong 1978; Huang et al. 1999). Some studies on infiltration rate and groundwater abundance were performed using hydrogeological methods like infiltration tests or pumping tests (Dai 1981; Li et al. 1999; Guo et al. 2000; Du et al. 2000), profiles of soil moisture and tritium in soil water (Zhang et al. 1990; Lin and Wei 2006) and groundwater level fluctuations (Yan and Wang 1983; Tang 1995; Tang et al. 1997). According to Tang (1995), the groundwater recharge amount from rain and irrigation cannot decrease with depth if the depth to water table exceeds 5 m. Through investigating groundwater fluctuations after a 107.5 mm rainstorm at a loess platform located in the northwest of the Weihe River, Tang et al. (1997) stated that the infiltration coefficient of precipitation decreases as the depth to water table increases.

Since groundwater recharge is jointly affected by rainfall pattern, human activities and local catchment characteristics, it is difficult but critical to identify the spatial heterogeneity in infiltration modes and recharge mechanisms at the catchment scales. Previous studies did provide a basic understanding of groundwater resources and their renewability over the Loess Plateau. However, the mechanisms governing groundwater recharge in the study area is still under dispute. It was considered that the groundwater recharge from precipitation increased by vertical fissures or macro-pore in loess layers cannot be thoroughly addressed only by studies at point or small watershed scales. By conducting infiltration tests, profiles of soil water content and its tritium isotopic content, some studies show that

macro-pore or vertical fissures in the loess layers will be filled up during infiltration processes and hardly increase precipitation infiltration (Du et al. 2000), and the rainfall infiltration has been proven to be a piston infiltration mode at a rate of about 0.3 m/a (Zhang et al. 1990; Lin and Wei 2006). On the contrary, through examining the groundwater level fluctuations of 24 pumping wells in the loess platform, Yan and Wang (1983) indicated that groundwater receives rapid recharge from precipitation primarily by crannies, cavities, solution passages or sinks, and the permeability coefficient shows a marked spatial variability.

Isotopic compositions of hydrogen and oxygen environmental isotopes ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) are widely used in hydrologic studies due to their conservative characteristic of moving with  $\text{H}_2\text{O}$  molecule. Under the combined effect of condensation and evaporation of water vapor,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  of precipitation shows isotopic effects such as altitude effect, rainfall amount effect, and seasonal effect (Mook 2000). These effects can be retained in groundwater. In areas where precipitation is a dominant recharge source, variations in groundwater isotopic compositions are determined by the infiltration rate and recharge amount, responding quickly to precipitation if there is a considerable recharge but becoming relatively steady when it recharges slowly (Eichinger et al. 1984; Mathieu and Bariac 1996). The discrepant fractionation rate of hydrogen and oxygen isotopes resulting from a difference in atomic weight will generate non-equilibrium isotope fractionation during evaporation or condensation. The extent of non-equilibrium is reflected by deuterium excess (*d-excess*) defined by Dansgaard (1964) as

$$d\text{-excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O} \quad (1)$$

Retaining spatio-temporal variations in hydrogen and oxygen isotopes in precipitation and groundwater, in conjunction with hydrologic observations and hydrochemistry, has been widely used to identify origins of water bodies (Vrbka et al. 1993; Lambs 2000), infiltration modes of precipitation (Douglas 1997; Gaziz and Feng 2004; Li et al. 2007), the interactions between groundwater and other waters (Simpson and Herczeg 1991; McDonnell et al. 1991; Mook 2000; Lamontagne et al. 2005; Song et al. 2006) and groundwater recharge mechanisms (Clark and Fritz 1997; Tang et al. 2001; McGuire et al. 2002; Rademacher et al. 2003; Demlie et al. 2007; Gates et al. 2008).

Limited isotopic studies have been performed in the Loess Plateau, mainly at profile or point scales. Wang (2007) investigated the groundwater recharge processes with hydrological observations and  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  in precipitation, soil water and groundwater at the Changwu Experimental Station in Shaanxi Province, and pointed out

that the groundwater at the platform of the Loess Plateau obtains recharge primarily from precipitation infiltration and low-lying landforms such as loess plates and ponds. However, few isotopic studies in the Hilly Loess Region of the Loess Plateau were performed.

The objectives of this study are to (1) examine spatio-temporal variations of precipitation and the isotopic compositions in precipitation and groundwater, (2) investigate the contributing factors and indications of precipitation isotopic compositions, and (3) identify the isotopic evidence of the origin of groundwater and its response to precipitation in the Hilly Loess Region of the Loess Plateau.

### Site descriptions

The Chabagou Catchment ranging in latitude between 37°38'N and 37°48'N and in longitude between 109°47'E and 110°02'E, located in the semi-arid Hilly Loess Region of the Loess Plateau, is the third tributary of the Yellow River (Fig. 1a). The area up the Caoping Hydrological Station (CHS) is 187 km<sup>2</sup>. Elevations decrease from the northwest of around 1,302 m to the southeast of around 898 m. Many side slopes near the drainage divide even exceed 50° and the average slope is roughly 21°, while the slope of the mainstream has an average gradient <0.009. According to observations at CHS by the Yellow River Conservancy Commission, the mean annual rainfall during 1959–2006 is about 400 mm, ranging from 218 to 636 mm, about 90% of which falls during the period from May to September. The average annual air temperature is observed to be 8°C with a range of between –27 and 38°C, with pan evaporation of about 1,200 mm and a frost period of nearly 180 days.

There exists extensive soil erosion in the study area caused by a sparse vegetation cover, intensive rainstorms, and irrational cultivation on sloping lands (Liu and Zhong 1978; Huang et al. 1999; Xia et al. 2007). Since the 1960s, silt arresters and terraces were built to decrease soil and water losses, and the volume capacity of silt arresters exceed  $33.1 \times 10^6$  m<sup>3</sup> (Song et al. 2009) up to the year 2001.

The geological map, as well as a geological cross-section, is illustrated in Fig. 2. The study area is mainly covered by Upper Pleistocene Malan Loess and Middle Pleistocene loess sediments (including Lishi Loess and alluvium), and the latter appears near the ditches due to serious erosion (Fig. 2a). The depth of loess layers varies from several meters near the ditches to over 100 m in the upper reaches. In the lower reaches of the study area, there exists the Triassic Yanchang Group mainly as Feldspar-rich sandstone (Fig. 2b). The shallow groundwater primarily exists in the water-bearing porous sediments and

fractured bedrocks (CAS 1990). Due to the rainfall patterns and underlying surface conditions like topography and land cover, most floods recede within several hours (10 h at most), and so groundwater cannot be readily recharged from continuous precipitation infiltration or surface runoff. The groundwater primarily discharges by domestic wells and springs (especially fissured springs). Domestic wells are usually drilled for about 20–90 m into the loess layers with a water depth of about 1–2 m, yielding a quantity of <1 m<sup>3</sup>/day; most fissured springs discharge at a rate of <1 L/s. The depth to water table varied in a range of 10–80 m, larger in the upper reaches and near the divide of the watershed.

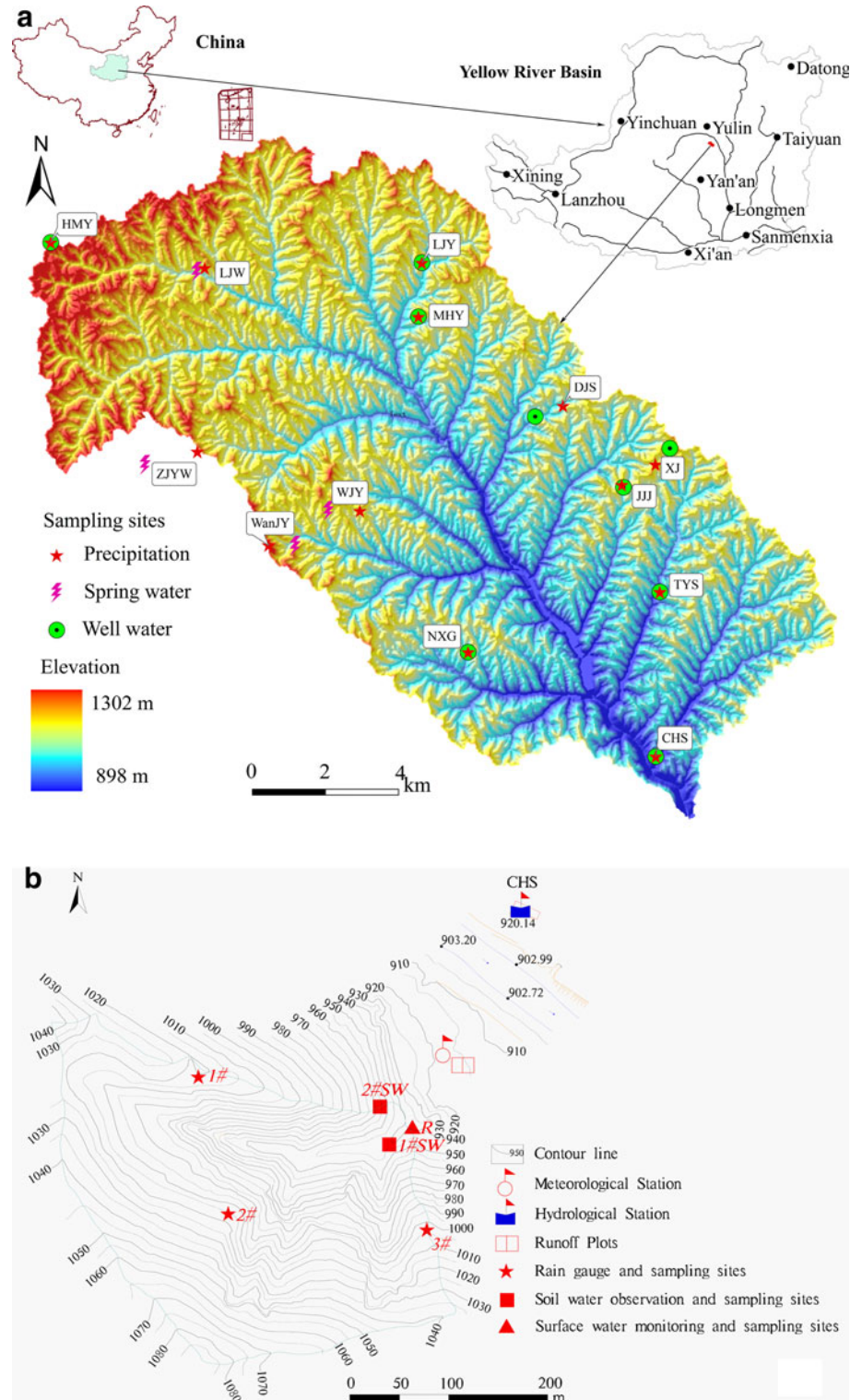
### Methods

The Chabagou Catchment was selected to monitor the hydrometeorological variables and collect water samples systematically at different spatio-temporal scales from May to October during the period 2004–2006. Precipitation at the 13 rain gauge stations in the Chabagou Catchment (Fig. 1a) and 3 stations in the Caopingxigou Experimental Watershed (CXEW) (Fig. 1b) were recorded using JDZ-1 rain-gauge data collector at an interval of 5 min. The 13 sites are Heminyan (HMY), Liujiawa (LJW), Lijiayan (LJY), Mahuyan (MHY), Zhujiayangwan (ZJYW), Wanjiayan (WanJY), Wangjiayan (WJY), Dujiashan (DJS), Jijajian (JJJ), Xiaoji (XJ), Taoyuanshan (TYS), Niuxuegou (NXG) and CHS. The surface runoff was observed at CHS every 10 days, and surface runoff during floods were sampled at five major points, i.e., on the point of rise, on the way to peak, peak discharge, recession and after recovery. Samples of monthly precipitation as well as groundwater (spring water or well water, Fig. 1a) were collected at the Chabagou Catchment from June in 2005.

Individual precipitations were collected immediately after each rain event and then mixed at the end of the month to form the monthly precipitation samples. Meteorological variables like air temperature, humidity and rainfall were observed at the Vantage Pro Meteorological Station every 10 min in CXEW since 2004. For a detailed investigation of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in individual precipitation at CXEW, precipitation larger than 5 mm was collected from 5 sites immediately after each rain event (Fig. 1b). Also, surface runoff processes were monitored manually at the CXEW. Surface water samples were also sampled at 5 stages of the rainfall-runoff processes. All of such samples were sealed in 50 or 100 ml airtight PVC bottles.

Totally 243 individual precipitation samples (including 14, 22 and 21 rain events at CXEW in 2004–2006, and 9 samples at the Chabagou Catchment), 198 monthly precipitation samples and 141 groundwater samples were

**Fig. 1** Location of the study area, sampling sites of precipitation and groundwater at the Chabagou Catchment (a) and experiment design at CXEW (b)

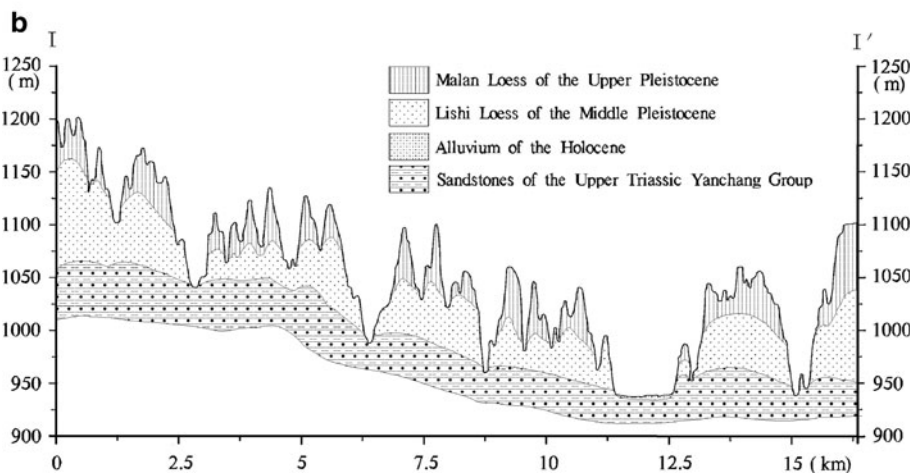
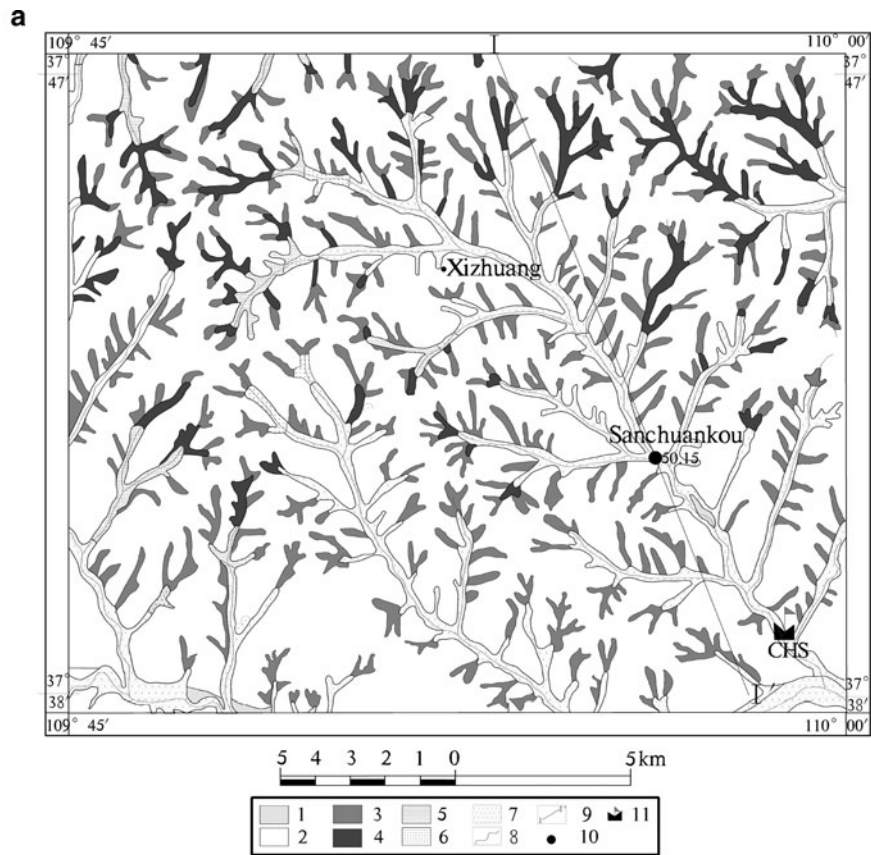


analyzed. The deuterium and oxygen-18 compositions were measured with isotopes mass spectrometer Finnigan Mat253 (USA) with TC/EA method (Li et al. 2007), expressed as  $\delta$  values in parts per mill relative to the Vienna Standard Mean Ocean Water (VSMOW). All the

isotopic measurements were analyzed in the Analysis Center of the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), Chinese Academy of Sciences. Analytical accuracy achieved  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 2\text{‰}$  for  $\delta^2\text{H}$ , respectively.



**Fig. 2** A geological map (a) and cross-section (b) of the Chabagou Catchment. The geological map is modified from the results of geological survey performed in 1979 (1:200,000). **a** 1 Holocene; 2 Upper Pleistocene; 3 Middle Pleistocene; 4 Pliocene; 5 Jurassic Yan'an Group; 6 Jurassic Fuxian Group; 7 Triassic; 8 Geological boundary; 9 Location of the cross-section; 10 Serial number and depth of the borehole; 11 Caoping Hydrological Station



**Results and discussion**

Spatio-temporal variations of precipitation

*Temporal variations*

The average annual rainfall ( $P_a$ ) observed at CXEW from 2004 to 2006 were 351.4, 356.0 and 519.5 mm, respectively, over 90% of which occurring from May to September. The number of days with rainfall larger than 1 mm

was 47, 38 and 49 days, and the maximum rainfall was 54.4, 46.4 and 100.8 mm (see *ESM\_1*). About 50% of  $P_a$  fell in July and August as heavy rains or rainstorms, with an instantaneous rainfall intensity larger than 60 mm/h and even 150–200 mm/h occasionally. During the 3 years, the maximum rainfall in 2, 6, and 24 h were 33, 52.8 and 100.2 mm, respectively, all taking place on 29 August 2006. According to a rainfall series of 45 years, the year 2004 and 2005 were considered an average year while the year 2006 was categorized into the wet year.

### Spatial variations

Taking into account the observation intervals and effectiveness of groundwater recharge, rainfall distributions at 2, 6 and 24 h scales for 11 rainstorms with a maximum point rainfall exceeding 50 mm at the Chabagou Catchment (Fig. 3), as well as the maximum rainfall in 3, 7 days and month scale (see in *ESM\_2*) were examined. Although using geostatistical interpolation methods would be a promising way to interpolate rainfall distributions across the Loess Plateau (Lin and Mo 2008), Ye (2007) indicated that there is no obvious difference in interpolation results if rain gauge stations are sufficiently dense. Here, the inverse distance weighting method was used. The spatial variations were depicted using the variation coefficient of areal rainfall ( $C_v$ ), ratio of maximum and minimum point rainfall ( $\alpha$ ) and non-uniform coefficient of rainfall ( $\eta$ , the ratio of average and the maximum rainfall) (Wang et al. 1999), and  $C_v$  is calculated as

$$C_v = \sqrt{\frac{\sum_{i=1}^n \left(\frac{H_i}{\bar{H}} - 1\right)^2}{n-1}} \quad (2)$$

where  $H_i$ ,  $\bar{H}$  denotes the point rainfall at each rain gauge stations and the average of point rainfall at the whole catchment, and  $n$  is the number of rain gauge stations.

Comparing the precipitation variations at 2, 6 or 24 h scales, it is indicated that the rainstorms show obvious spatial variability at a 200 km<sup>2</sup> spatial scale. As shown in Fig. 3a, the spatial variability of the maximum rainfall in 2 h was the most prominent, with  $C_v$ ,  $\alpha$ ,  $\eta$  being in the ranges of 0.27–0.94, 1.90–64.75, 0.30–0.74, respectively.  $H_{\max}$  in 2 h during the 3 years was 62.2 mm (19 August 2004), 51.4 mm (2 August 2005) and 40.2 mm (30 July 2006). At longer time scales, the spatial variability decreases by certain degree but not much (Fig. 3b, c). In the 3 years, the maximum point rainfall were 96.0, 76.0 and 100.4 mm, and all occurred in August with obvious spatial variations (Fig. 3c). Relatively, long-duration rainstorms have a weaker variability with  $\eta$  between 0.43 and 0.92. In general, the larger the rainfall intensity is, the shorter duration the precipitation lasts and the smaller area it covers (Zhang 1983).

The maximum rainfall in continuous 3 days averaged 63.1, 56.7 and 106.5 mm in the 3 years with extreme differences to be 65.8, 37.2 and 17.2 mm, while the average of maximum rainfall in 7 days was 74.3, 93.4 and 131.8 mm, respectively, all showing ranges larger than 60 mm (see *ESM\_2*). For monthly rainfall ( $P_m$ ), there was still an obvious variability (with  $\alpha$  being as high as 1.33–3.56) especially in June and August (see *ESM\_3*). The accumulated rainfall from May to October ( $P_{5-10}$ ) during the 3 years showed the values of  $\alpha$  to be as large as

1.34, 1.46 and 1.22. The maximum ratio of rainfall in July and August ( $P_{7-8}$ ) to  $P_{5-10}$  occurred at LJY (73%), ZJYW (63%) and NXG (65%). The precipitation center was located in the upper and/or middle reaches for 2004 and 2005, and it shifted to the lower reaches in 2006. On all accounts, the comparisons at different time scales suggest precipitation in the study area shows the most notable variability in the Loess Plateau (Wang et al. 1999).

### Localized rains

To calculate the proportion of localized rains, moderate rain or light rain with  $\alpha \geq 5$  and/or heavy rain or rainstorm with  $\alpha \geq 2$  were defined to be localized rain. In 2005, there were 32 localized rains from May to October and their accumulated rainfall (206.5 mm) accounted for 55% of  $P_{5-10}$ , among which 8 localized storms in July and August amounted to 40% of  $P_{5-10}$ . In 2006, 28 localized rains (40% of  $P_{5-10}$ ) were detected and the 5 localized storms amounted to 24% of  $P_{5-10}$ . There are about 4–5 localized rains in each month. The large frequency of localized rains (particularly for rainstorms) and their spatial variability suggest that localized convective rains are too pronounced to be negligible in the study area.

### Spatio-temporal variations of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation

#### At CXEW

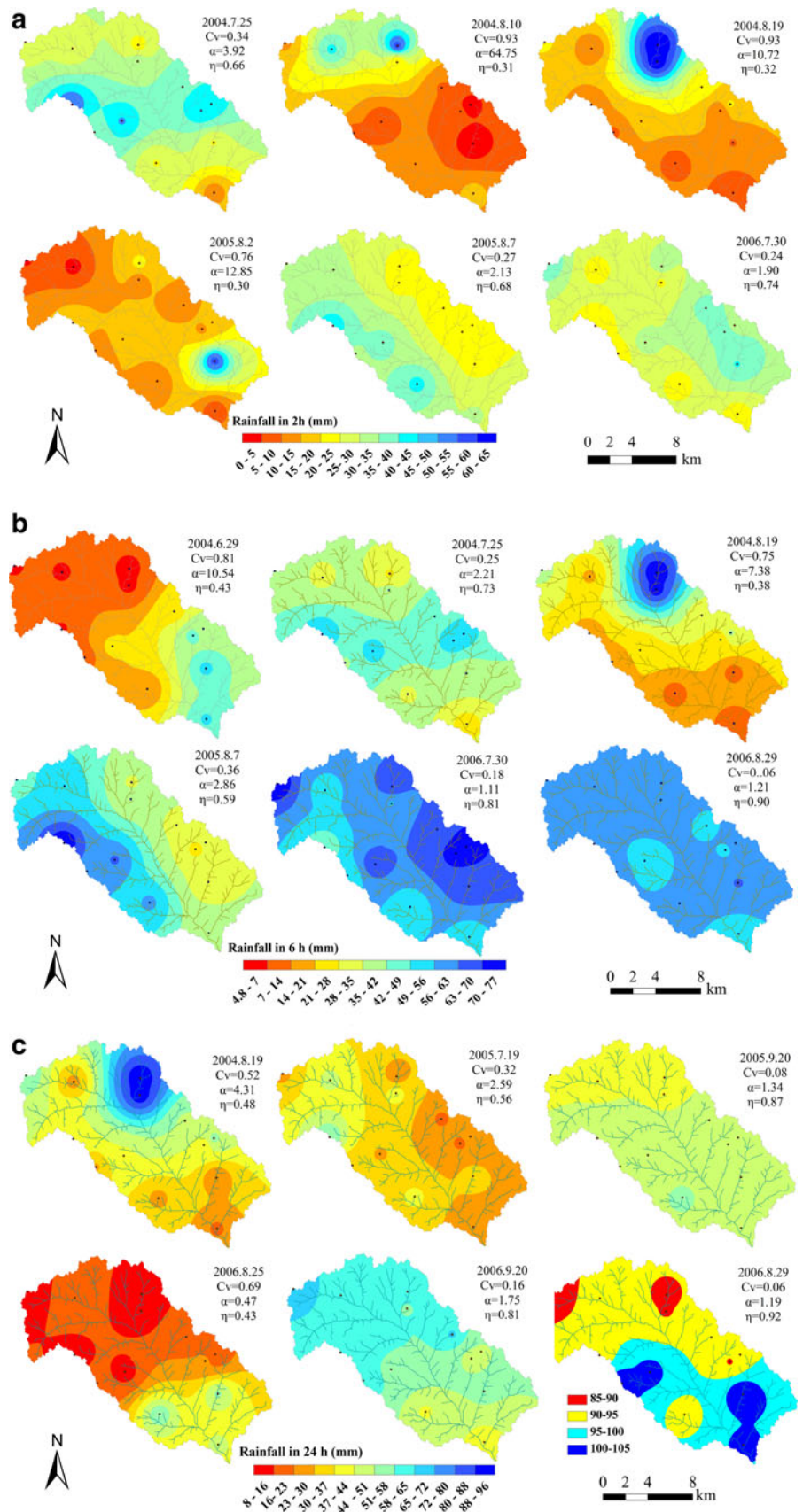
Isotopic compositions in individual precipitations varied greatly in the 3 years, with  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ranging from  $-16.16$  to  $4.87\text{‰}$  and  $-115.7$  to  $13.1\text{‰}$ , respectively (Fig. 4). The range of  $\delta$  values and the meteoric water lines (MWL) are listed in Table 1. Precipitation isotopic compositions showed seasonal patterns, which were enriched in May and June, depleted in July and August (between  $-80$  and  $-60\text{‰}$  for  $\delta^2\text{H}$ ) and more depleted in September. The *d-excess* varied between  $-18.8$  and  $18.4\text{‰}$ , and it exceeds  $7.5\text{‰}$  for heavy rains (Fig. 4).

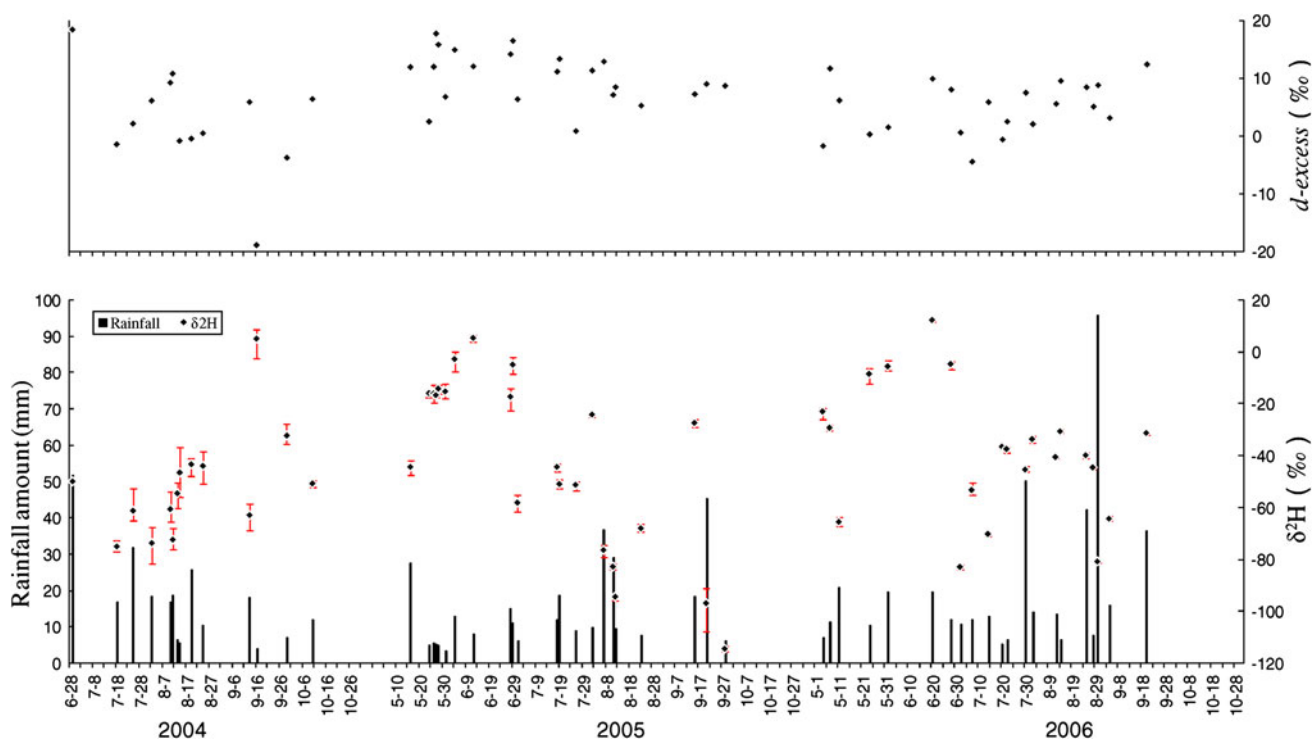
The spatial variability in precipitation isotopic compositions at CXEW existed but it decreased gradually during 2004–2006. As shown in Fig. 4, the range of  $\delta^2\text{H}$  in 2004 was as large as  $10\text{‰}$  for most rain events, whereas in 2005 the variability mainly existed in May and June, and as for the wet year 2006, only weak spatial variations were displayed.

#### At Chabagou Catchment

Merlivat and Jouzel (1979) and Harvey (2005) revealed that monthly precipitation samples with *d-excess*  $< 3\text{‰}$  may be indicative of evaporation when raindrops falling

**Fig. 3** Rainfall distributions for storms in 2 h (a), 6 h (b) and 24 h (c) at the Chabagou Catchment in 2004–2006





**Fig. 4** Average  $\delta^2\text{H}$  and  $d\text{-excess}$  of rain events (>5 mm) from May to October, 2004–2006 at CXEW

**Table 1** Range of  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  in precipitation and MWLs in 2004–2006

Year	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}-\delta^{18}\text{O}$	$n$	$R^2$
CXEW					
2004	−81.7 to 8.5	−10.89 to 4.90	$\delta^2\text{H} = 5.91 \times \delta^{18}\text{O} - 11.9$	61	0.929
2005	−115.7 to 12.9	−16.16 to 1.07	$\delta^2\text{H} = 8.06 \times \delta^{18}\text{O} + 10.3$	110	0.963
2006	−83.0 to 12.3	−11.21 to 0.30	$\delta^2\text{H} = 7.86 \times \delta^{18}\text{O} + 4.1$	63	0.963
2004–2006			$\delta^2\text{H} = 7.55 \times \delta^{18}\text{O} + 3.3$	243	0.932
Chabagou Catchment					
2004	−80.8 to −30.7	−11.05 to −4.48	$\delta^2\text{H} = 7.38 \times \delta^{18}\text{O} + 1.0$	34	0.940
2005	−83.8 to −1.8	−11.49 to 0.17	$\delta^2\text{H} = 7.76 \times \delta^{18}\text{O} + 7.0$	72	0.956
2006	−69.8 to 11.7	−10.41 to 1.03	$\delta^2\text{H} = 7.51 \times \delta^{18}\text{O} + 3.7$	29	0.989
2004–2006			$\delta^2\text{H} = 7.69 \times \delta^{18}\text{O} + 5.3$	135	0.964

down or before collection, thus they should be discarded. Given the semi-arid climate of the study area, monthly precipitation samples with negative  $d\text{-excess}$  were not taken into account. Since the effect of light rains can be smoothed effectively, the seasonal effect of isotopic compositions in monthly precipitation was strengthened. The  $d\text{-excess}$  in monthly precipitation varied between 0.9 and 19.9‰, most between 6 and 10‰. The isotopic compositions in monthly precipitation were similar to that in Xi'an City examined by the International Atomic Energy Agency (IAEA) in 1985–1992, i.e., the rainfall amount weighted  $\delta^2\text{H}$  was peaked in April and decreased from May to September; the  $d\text{-excess}$  varied in the range of 7.4–21.9‰ and it increased from 7.4‰ in May to 16.9‰ in August.

The spatial variability of isotopic compositions ( $\delta^2\text{H}$  and  $d\text{-excess}$ ) at the Chabagou Catchment were much pronounced, even in the rainiest August (see *ESM\_4*).

#### Correlations between precipitation isotopic compositions and meteorological variables

Precipitation isotopic compositions show some rainfall amount effect which differs before and after September. Figure 5 demonstrates the  $\delta-P$  relationship for individual precipitation (Fig. 5a) and monthly precipitation (Fig. 5b). As shown in Fig. 5a, the upper limit of  $\delta^2\text{H}$  for individual precipitations from May to August (Aug) decreased with increases of rainfall amount, and  $\delta^2\text{H}$  for heavy rains



(>25 mm) was mainly lower than  $-50\text{‰}$ ; whereas in September (Sep) and October (Oct), it was more depleted than the precipitations with similar rainfall. The rainfall amount effect for individual precipitation in 2004 and 2005 ( $\delta^2\text{H} = -1.70 \times P - 17.2$  for  $P < 50$  mm, Liu et al. 2007a) was more significant than that in 2006. The  $\delta^2\text{H}-P_m$  correlation from May to August was  $\delta^2\text{H} = -38.68 \times \ln(P_m) + 128.4$  with a  $R^2$  of 0.606, however, there was still no obvious rainfall amount effect in autumn, which is similar to that of event rainfall (Fig. 5b).

Since the precipitation isotopic compositions are controlled by the fractionation effect during vapor evaporation, condensation, transportation and penetration of raindrops, they are usually well correlated with meteorological variables (e.g., Dansgaard 1964; Gat 1996). However, poor correlation between precipitation  $\delta$  values and surface air temperature ( $T_s$ ) were found at CXEW. The reason for that could be ascribed to (1) the difference between  $T_s$  and the upper air temperature and (2) the narrow range of  $T_s$ . Similarly, there was no significant correlation between  $\delta$  values and the relative humidity of the surface air ( $h_r$ ). In 2005, the best cross-correlation function (CCF) appeared between  $\delta^2\text{H}$  and  $h_r$  10 days before ( $h_{r(10)}$ ), i.e.,  $\delta^2\text{H} = 4.3 - 1.490 \times h_{r(10)}$  (with CCF  $-0.635$ ), while the  $\delta-h_r$  correlation disappeared in 2006. Precipitation isotopic compositions in the 3 years showed a multivariate linear relationship with  $P$ ,  $T_s$  and  $h_r$  4 days before ( $h_{r(4)}$ ), i.e.,  $\delta^2\text{H} = -0.766 \times t_{(4)} - 0.958 h_{(4)} - 0.424 \times P + 40.5$  with a  $R^2$  0.373 and  $n$  of 52. From the analysis above, precipitation isotopic compositions, particularly in summer, are found to be dominated by rainfall amount and affected by temperature and mixing processes of water vapor during raindrops formation.

Indications of precipitation isotopic compositions

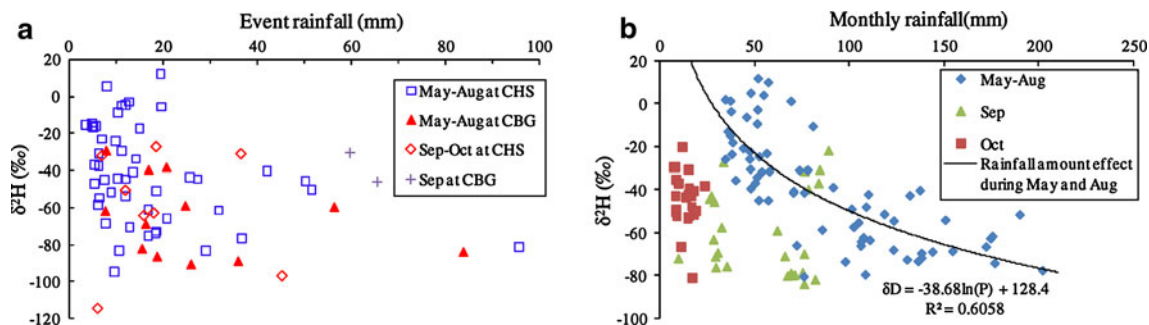
Indications of isotopic compositions in individual precipitation

The different rainfall amount effect in summer and autumn, either for individual or monthly precipitation, suggests that

$\delta$  values of summer precipitation are mainly affected by rainfall amount, and in autumn it is determined by other factors as vapor sources, temperature and evaporation of raindrops. As shown in Fig. 5a, not all the heavy rains showed depleted  $\delta$  values, and light rains could have depleted heavy isotopes occasionally. This would be indicative of different sources of water vapor and changing hydrologic processes during vapor condensation, transportation and falling down. The more depleted isotopic compositions in precipitation during September indicates that the heavy isotopes in water vapor have penetrated preferentially with the strengthening of cold air from the north and with the withdrawing of summer monsoon (Liu et al. 2007a). Meanwhile, the enriched  $\delta$  values of some rains in September, e.g., a rain event of 4 mm in 14 h with positive  $\delta$  values and the minimum  $d$ -excess ( $-18.8\text{‰}$ ) on 16 September 2004, suggest strong re-evaporation during penetration.

Isotopic evidence of monsoon intensity

The spatio-temporal variations of precipitation isotopic compositions indicate differences in water vapor origin, monsoon intensity and hydrological processes that water vapor and raindrops experience. As illustrated in Fig. 4, precipitation isotopic compositions at the  $0.1 \text{ km}^2$  CXEW showed different spatial patterns in the 3 years. The range of  $\delta^2\text{H}$  in 2004 was larger than  $10\text{‰}$  while it was smaller than  $2\text{‰}$  in 2006. There were similar patterns for the MWLs at CXEW. The slopes of MWLs at 5 sites in 2004 (5.42–6.55) and 2005 (7.63–8.57) varied more significantly than that in 2006 (7.75–8.02) (Liu et al. 2007a). Compared to the marked variations in precipitation isotopic compositions and in MWLs at CXEW in 2004–2005, the weak variability in 2006 suggests a stronger monsoon intensity (Liu et al. 2007b; Lin et al. 2009) which transported well-mixing vapor to decrease the spatial variability. This is also validated by the facts mentioned above: (1) there were more localized rains and a more significant rainfall amount effect in 2004 and 2005, and (2) there was slight altitude



**Fig. 5** Rainfall amount effect of  $\delta^2\text{H}$  in event rainfall of CXEW (a) and monthly rainfall at the Chabagou Catchment (b) from May to October, 2004–2006

effect for rainfall-weighted  $\delta^2\text{H}$  in 2004–2005 but not in 2006.

#### Indications of the meteoric water lines

As shown in Table 1, the slopes of MWLs derived from rain samples at CXEW in a specific year showed great variations, lowest in 2004 and highest in 2005 (8.06), suggesting that most precipitation encountered relatively severe re-evaporation during longer-duration rainfall processes in 2004 while it mainly experienced equilibrium fractionation in 2005. The MWL from all the individual precipitations in 2004–2006 was  $\delta^2\text{H} = 7.55 \times \delta^{18}\text{O} + 3.3$  with a  $R^2$  of 0.932 and  $n$  of 243. Therefore, although the MWL of a specific year can be well indicative of the water vapor origin and climatic or meteorological variables, it is inadequate to reflect climatic or physical geographical characteristics of the study area at a longer timescale due to its instability.

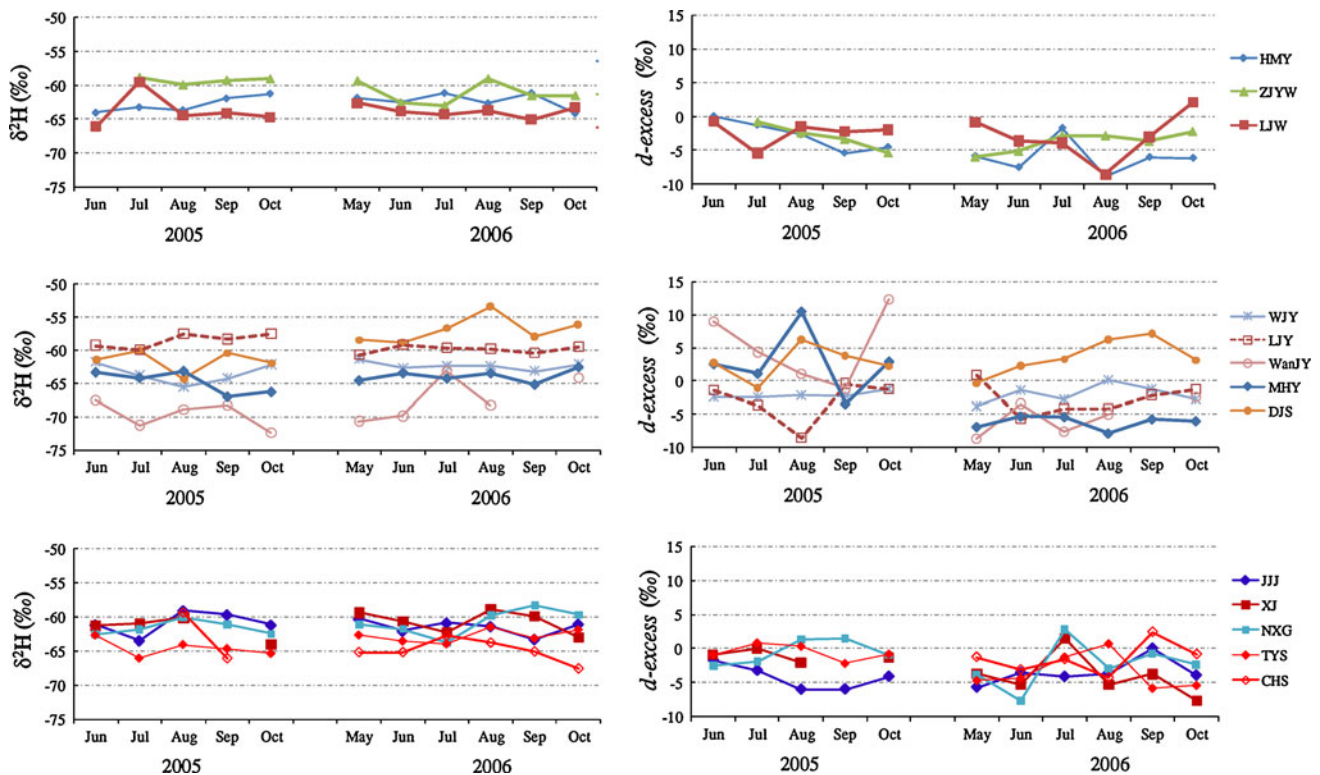
Notably, the MWLs calculated from monthly precipitation in the Chabagou Catchment during the 3 years (with slopes between 7.38 and 7.76) were steadier than that from individual precipitations in a specific year, and close to MWLs derived from all the individual precipitations (slope = 7.55, Table 1). Comparisons of MWLs show that the isotopic compositions of monthly precipitation well integrate the effects of rainfall amount, elevation and temperature. Moreover, the MWL from all the monthly

precipitation ( $\delta^2\text{H} = 7.69 \times \delta^{18}\text{O} + 5.3$ ) was close to local meteoric water line (LMWL)  $\delta^2\text{H} = 7.57 \times \delta^{18}\text{O} + 3.9$  ( $R^2 = 0.9403$ ,  $n = 369$ ) that was calculated from all the precipitation samples at the two watersheds, and also similar to the LMWL of Xi'an City during 1985–1992 ( $\delta^2\text{H} = 7.49 \times \delta^{18}\text{O} + 6.1$ ,  $R^2 = 0.92$ ,  $n = 60$ ). From this meaning, LMWL is a good indicator of climatic signals (such as air temperature, humidity, rainfall amount and vapor origin) and local geographical variables (e.g., location, elevation and continentality). Therefore, special attentions should be paid to selecting representative LMWL to well reflect local climatic or geographical variables in the absence of long-term monitoring of isotopic compositions in ungauged areas.

It is worth to mentioning that, as revealed in Table 1 and Liu et al. (2007a), although MWLs varied annually, the intercept ( $d$ ) changed with the slope ( $S$ ) with a functional relation  $9.74 \times S - d = 69.3$ , i.e., the MWLs intersected at about  $(-9.7, -69\text{‰})$  in the  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  plot. This indicates that precipitation in the study area has similar vapor sources with isotopic compositions around  $(-9.7, -69\text{‰})$ .

#### $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in shallow groundwater

Variations of  $\delta^2\text{H}$  and  $d$ -excess in groundwater in 2005–2006 are shown in Fig. 6. The average, standard deviation (*stdev*) and the difference between  $\delta$  values in



**Fig. 6** Temporal variations of  $\delta^2\text{H}$  and  $d$ -excess in groundwater at the Chabagou Catchment

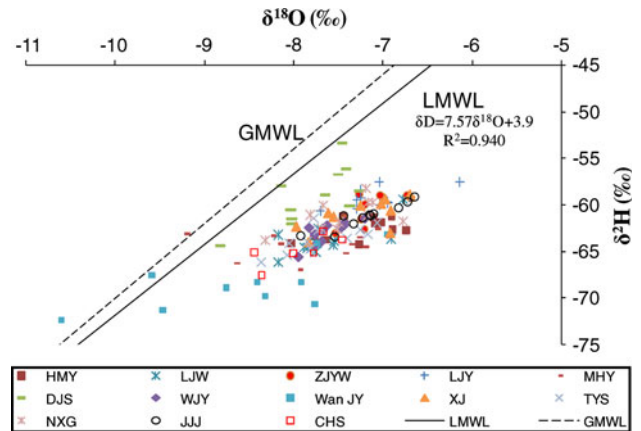
May of 2006 and that in October of 2005,  $\Delta_D$  or  $\Delta_O$ ) for  $\delta^2H$  and  $\delta^{18}O$  are shown in Table 2. Groundwater isotopic compositions ranged between  $-10.59$  and  $-6.13\text{‰}$  for  $\delta^{18}O$ , and between  $-72.4$  and  $-53.4\text{‰}$  for  $\delta^2H$ , amounting to 21% and 15% of the range of isotopic compositions in individual precipitations, respectively.

Groundwater isotopic compositions in the upper and lower reaches seemed more steady than that in the middle reaches (Fig. 6), and it was most concentrated at LJY and most depleted at WanJY. The groundwater isotopic compositions in the upper reaches showed weak variation except at the spring of LJW, while in the lower reaches,  $\Delta$  varied obviously at XJ ( $\Delta_O > 0.8\text{‰}$ ) and TYS ( $\Delta_D = 4.6\text{‰}$ ). Distinct variations of  $\delta$  values were detected in the middle reaches with the range of  $\delta^2H$  exceeding 9–11‰ and 2.83‰ for  $\delta^{18}O$ . The groundwater *d-excess* varied between  $-8.8$  and  $12.3\text{‰}$ , changing obviously at sites MHY, DJS, LJY, WanJY and LJW. The groundwater line ( $\delta^2H-\delta^{18}O$  relationship) was  $\delta^2H = 3.22 \times \delta^{18}O - 38.1$  ( $R^2 = 0.454$ ,  $n = 135$ ). As the  $\delta^2H-\delta^{18}O$  plot illustrates (Fig. 7), isotopic compositions of most groundwater deviate significantly from LMWL, and groundwater at sites WanJY, DJS and MHY were located close to LMWL in some months.

Groundwater origin and its response to precipitation

Origin of shallow groundwater

Contrary to the obvious seasonality of precipitation and its isotopic compositions, the range of  $\delta$  values in groundwater was largely decreased to be 15–21% of that in individual



**Fig. 7**  $\delta^2H-\delta^{18}O$  plot of precipitation and groundwater at the Chabagou Catchment Legend: the significant deviation of most groundwater from LMWL illustrates severe evaporation of groundwater before reaching the water table.  $\delta$  values of groundwater at WanJY, DJS and MHY have pronounced variations, and  $\delta^2H-\delta^{18}O$  plot of groundwater occasionally lies around the LMWL, suggesting a recharge from precipitation or storm runoff which avoid obvious evaporation

precipitations from May to October (Table 2). Also, the groundwater line was much lower than LMWL (Fig. 7) and intersected with LMWL at around  $(-9.66, -69.2\text{‰})$ , close to the isotopic compositions of the origin of precipitation. The isotopic results showed that groundwater ultimately originates from precipitation, and most has experienced severe evaporation before reaching the water table.

Since the depth to water table in the study area exceeds the evaporation limit of groundwater (4.5–6.3 m for bare land and winter wheat, Huang et al. 2007), obvious changes of groundwater *d-excess* most likely resulted from new

**Table 2** Statistics of  $\delta^2H$ ,  $\delta^{18}O$  in groundwater in the period 2004–2006 at the Chabagou Catchment

Sites	Elevation (m)	Range/‰	Average/‰	stdev/‰	$\Delta_D$ , $\Delta_O$ /‰
Upper					
HMY	1,253	3.0/1.28	$-62.59/-7.26$	1.55/0.41	$-0.6/0.09$
ZJYW	1,140	6.6/1.40	$-60.46/-7.13$	1.61/0.27	$-0.3/0.04$
LJW	1,071	3.1/1.57	$-63.79/-7.64$	1.70/0.45	2.1/0.12
Middle reaches					
WJY	1,119	4.4/2.26	$-62.93/-7.61$	1.23/0.21	0.8/0.42
LJY	1,065	4.2/0.85	$-59.29/-7.05$	1.04/0.40	$-3.1/-0.66$
WanJY	1,065	4.2/0.74	$-68.47/-8.55$	2.94/1.08	1.7/2.83
MHY	1,067	9.2/3.64	$-64.35/-7.77$	1.36/0.73	1.7/1.44
DJS	1,002	11.0/1.56	$-59.12/-7.79$	3.06/0.47	3.5/0.76
Lower reaches					
JJJ	1,072	5.1/1.27	$-61.27/-7.18$	1.34/0.38	0.9/0.31
XJ	1,060	4.6/1.30	$-61.06/-7.27$	1.63/0.44	4.6/0.86
NXG	1,018	5.5/1.55	$-61.15/-7.44$	1.57/0.42	1.4/0.53
TYS	971	4.4/1.28	$-63.63/-7.68$	1.41/0.41	2.7/0.82
CHS	910	8.2/1.22	$-64.96/-7.95$	1.63/0.39	

$-62.59/-7.26$  stands for  $\delta^2H$  and  $\delta^{18}O$  in permil;  
 $\Delta_D = \delta^2H_{200605} - \delta^2H_{200510}$ ,  
 $\Delta_O = \delta^{18}O_{200605} - \delta^{18}O_{200510}$

sources. Therefore, it is effective in identifying the processes of groundwater recharge in the semi-arid regions, where the evaporation of groundwater sources is significant.

#### Groundwater recharge in the middle reaches

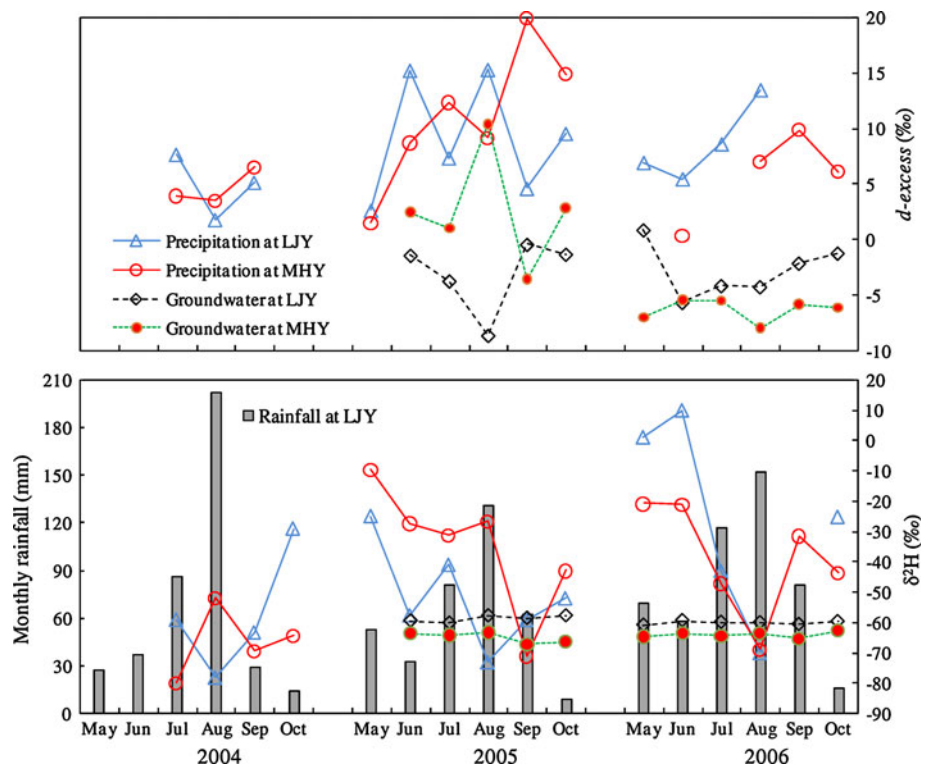
Seen from Fig. 6, *d-excess* varied significantly or changed quickly at some months (especially in July and August) at the sites LJY (−8.6 to 0.9‰), MHY (−7.9 to 10.5‰), DJS (−1.1 to 7.1‰) and WanJY (−8.6 to 12.3‰). This greatly differs from the positive *d-excess* of monthly precipitation and higher *d-excess* in heavy rains or rainstorms (>7.5‰, Fig. 4). Therefore, a fast decline in *d-excess* indicated that new sources of groundwater have evaporated substantially, while a fast increase of *d-excess* suggested new recharge from precipitation or storm runoff. For example, the  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  plot of some groundwater at WanJY, MHY and DJS were located close to the LMWL (Fig. 7), indicating that they can obtain recharge from channel precipitation or rainstorm runoff at some months. Herein, we take the four sites in the middle reaches as example to analyze the primary processes of groundwater recharge.

The sampling well at DJS was drilled 16 m into the valley. There are two silt arresters in the upper reaches of the well. One is 30 m upper and partly damaged, and the other is about 300 m upper which can effectively hold surface runoff. The location of the well and the existence of

silt arresters both facilitate groundwater recharge. Hence, the  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  plot and positive *d-excess* at DJS illustrates the evidence of recharge from channel precipitation or precipitation runoff hold up by the silt arresters, which was mainly in the form of vertical infiltration or lateral recharge. The deduction can be proved by the higher  $\delta^2\text{H}$  in 2006, which was in accordance with the concentrated  $\delta^2\text{H}$  in individual precipitation (Fig. 4). The groundwater isotopic compositions at the spring of WanJY may also indicate the similar hydrological processes, i.e., groundwater obtained recharge from storm runoff which was reflected by the altitude effect of precipitation isotopic compositions.

In order to examine the lag time of groundwater to precipitation,  $\delta^2\text{H}$  and *d-excess* in monthly precipitation and groundwater at sites MHY and LJY are compared in Fig. 8. At MHY, a fast increase of *d-excess* for groundwater in August of 2005 suggested a new sources whose *d-excess* (>10.5‰) was characterized by precipitation or storm runoff in August 2005. However, the decline in *d-excess* in September 2005 indicated the recharge of severe-evaporated sources either by lateral recharge or by surface runoff retained by silt arresters. Meanwhile, at the well of LJY, *d-excess* increased in September 2005 and declined significantly in June 2006 (Fig. 8), reflecting two opposite recharge processes: groundwater gained remarkable contributions of evaporated recharge with low *d-excess* in August in 2005 or June in 2006, and it obtained mildly-evaporated recharge in September in 2005. It should

**Fig. 8** Comparisons of  $\delta^2\text{H}$  and *d-excess* in precipitation and groundwater at LJY and MHY





be noted that the variations of *d-excess* in groundwater at sites of LJY, WanJY and MHY in 2006 was smaller than that in the average year 2005, indicating that the recharge processes of groundwater are very complex. Detailed recharge processes across the watershed should be further examined combining with field investigation, hydrochemistry and groundwater monitoring.

## Conclusions

By hydrometeorological observations and sampling for precipitation and shallow groundwater at the Chabagou Catchment from May to October during 2004–2006, spatio-temporal variations of precipitation,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  in precipitation and groundwater were systematically examined. It can be concluded that:

1. Most pronounced spatial variability were observed in precipitation at different timescales in the study area, and over 90% of rainfall falls from May to September mainly as intensive rainstorms. There are about 3–4 heavy rains or rainstorms and 6–13 moderate rains in each year, accounting for 60–87% of annual rainfall.
2. The seasonality and spatial variability in precipitation isotopic compositions, as well as their contributing factors and indications, were revealed. The precipitation isotopic compositions are essentially enriched in May and June and depleted since July, and rainfall amount is a dominant contributing factor. The *d-excess* of heavy rainfall is larger than 7.5‰. The spatial variability in precipitation and its isotopic compositions suggests different monsoon intensity and hydrological processes. The LMWL is  $\delta^2\text{H} = 7.57 \times \delta^{18}\text{O} + 3.9$ , and the hydrogen and oxygen isotopic compositions of the precipitation origin is  $-9.7$  and  $-69$ ‰, respectively.
3. The origin of groundwater and the primary recharge processes in the middle reaches were identified. The groundwater line is  $\delta^2\text{H} = 3.22 \times \delta^{18}\text{O} - 38.1$  and intersects with LMWL at  $(-9.66$ ‰,  $69.2$ ‰). The isotopic compositions reveal that groundwater originates from precipitation and most experiences severe evaporation.  $\delta$  values in groundwater vary greatly in the middle reaches especially near the valleys, on the basis of which the varying sources and primary processes of groundwater recharge were identified.

The analysis of spatio-temporal variations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in precipitation and groundwater would provide a significant basis for detailed studies on the mechanisms governing shallow groundwater recharge in the study area, in which the hydrochemistry and groundwater level fluctuations could be integrated.

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