

Estimation of evaporation losses based on stable isotopes of stream water in a mountain watershed

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Abstract Water stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) can record surface water evaporation, which is an important hydrological process for understanding watershed structure and function evolution. However, the isotopic estimation of water evaporation losses in the mountain watersheds remains poorly explored, which hinders understanding spatial variations of hydrological processes and their relationships with the temperature and vegetation. Here we investigated $\delta^2\text{H}$, $\delta^{18}\text{O}$, and *d-excess* values of stream water along an altitude gradient of 2130 to 3380 m in Guan'egou mountain watershed at the east edge of the Qinghai-Tibet Plateau in China. The mean $\delta^2\text{H}$ ($-69.6\text{‰} \pm 2.6\text{‰}$), $\delta^{18}\text{O}$ ($-10.7\text{‰} \pm 0.3\text{‰}$), and *d-excess* values ($16.0\text{‰} \pm 1.4\text{‰}$) of stream water indicate the inland moisture as the major source of precipitation in study area. Water stable isotopes increase linearly with decreasing altitudes, based on which we estimated the fractions of water evaporation losses along with the altitude and their variations in different vegetations. This study

provides an isotopic evaluation method of water evaporation status in mountain watersheds, the results are useful for further understanding the relationship between hydrological processes and ecosystem function under the changing climate surrounding the Qinghai-Tibet Plateau.

Keywords Water stable isotopes · Mountain watersheds · Water evaporation losses · Altitude effect · Rayleigh fractionation

1 Introduction

Terrestrial water evaporation is an important hydrological process that affects water balance and energy conversion in different landscapes (Edwards et al. 2015; Gibson et al. 1993; Skrzypek et al. 2015). Therefore, it is crucial to elucidate surface water evaporation losses and their spatiotemporal variations for a better understanding of regional environmental evolutions under global change (Chahine 1992; Fan et al. 2019; Yang et al. 2011).

While mountains cover only one-fourth of land surface, more than half of runoffs in the world originate from mountains (Körner 2007; Marston 2008). Hydrological processes in the mountain watersheds can influence biogeochemical processes of nutrients and their coupling with the water availability, which subsequently have implications for the carbon sequestration, vegetation succession, and climate on the continent (Edwards et al. 2015; Fan et al. 2019; McGuire and McDonnell 2007). However, the understandings of hydrological processes in the mountain watersheds are still limited due to insufficient information on the meteorology and the hydrology (Brown and Pasternack 2014; Fan et al. 2019; Wen et al. 2012; Wu et al. 2019a). Especially, heterogeneous terrain and climate

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can change water flow and discharge pathways, and subsequently influence water evaporation within the mixing and transformation between precipitation, snowmelt, surface runoff, and groundwater (Beria et al. 2018; Jiao et al. 2019; Wassenaar et al. 2011; Xing et al. 2015). Therefore, although it is well known that hydrological processes in mountain watersheds might vary with the altitude by the temperature effect (Li et al. 2016; Shen and Poulsen 2019; Wen et al. 2012), mechanisms of vertical variations of the water evaporation losses remain unclear in many mountain watersheds, which hindered the accurate estimations of the regional water evaporation fluxes and the understandings of effects of hydrological processes on ecosystem structure and function in responses to climate change (Fan et al. 2019; Wen et al. 2012).

Because of distinct fractionation effects during evaporation, signatures of water stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are useful evidence on water sources and evaporation status (Cappa et al. 2003; Clark and Fritz 1997; Gat 1996; Gibson et al. 1993; McGuire and McDonnell 2007). The Global Meteoric Water Line (GMWL, $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$) has been expressed by the regression relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation on the global scale (Craig 1961). Thus, the water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, and the deuterium excess values ($d\text{-excess} = \delta^2\text{H} - 8\delta^{18}\text{O}$, Eq. 3) that mainly generated by the disequilibrium isotope fractionation of H and O could provide crucial information on moisture sources of precipitation (Dansgaard 1964; Tian et al. 2007; Yao et al. 2013). While plant transpiration and soil infiltration do not produce substantial isotope fractionation effect, the $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $d\text{-excess}$ values had been used to estimate water evaporation losses by combining with the isotopic fractionations in evaporation, and the isotopic mass balance of water input and output (Cui et al. 2017; Gibson et al. 2016, 1993; Gibson and Edwards 2002; Skrzypek et al. 2015). However, variations of isotope fractionation effects with the altitude by the temperature effect might raise uncertainties on the evaluation of land surface evaporation fluxes in the mountain regions (Wen et al. 2012; Yang et al. 2009).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of surface water flows generally increased with decreasing altitudes in the mountain watersheds (Hren et al. 2009; Ren et al. 2017; Wen et al. 2012; Wu et al. 2019a), which was mainly related to the gradual depletion of ^2H , ^{18}O in precipitation during the moisture condensation and rain out with decreasing temperatures according to the Rayleigh equation (Jiao et al. 2019; Shen and Poulsen 2019). However, it remains unclear whether and how the altitude effects of surface water flow isotopes in a mountain watershed were controlled by the variation of water evaporation losses (Shen and Poulsen 2019; Yang et al. 2011). Therefore, the estimation of water evaporation losses from surface water

flows with the altitude in a mountain watershed by using water stable isotopes has important implications for understanding regional water balance and its responses to climate change in mountain ecosystems (Gibson and Reid 2010; Jasechko et al. 2013; Skrzypek et al. 2015).

Basing on the above context, this study analyzed the $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $d\text{-excess}$ values of stream water and its variations along an altitude gradient in the Guan'egou mountain watershed of western China. Our objectives are: (1) to explore the major water recharge source, and how abiotic and biotic traits in the watershed scale influence the isotopic variations of stream water. (2) to estimate the fractions of water evaporation losses and their variations with the altitude, temperature, and vegetation. The information can enrich the knowledge of hydrological processes in mountain watersheds, and the application of water isotopes in ecological processes.

2 Materials and methods

2.1 Study area

The study was conducted in the Guan'egou watershed of Tanchang county, Gansu province at the east edge of the Qinghai-Tibet Plateau (QTP) in China ($104^\circ 19' \text{E} \sim 104^\circ 24' \text{E}$, $34^\circ 03' \text{N} \sim 33^\circ 53' \text{N}$) (Fig. 1a). The total area of the study watershed covers nearly 350 km^2 with a range of altitude from 1780 to 4154 m (Fig. 1b). The climate in the study watershed is dominated by a temperate continental climate where the mean annual temperature (MAT) and mean annual precipitation (MAP) are nearly 9.3°C and 640 mm, respectively. The air temperature varied with the altitude in the study watershed and showed an estimated vertical lapse rate of $0.53^\circ \text{C}/100 \text{ m}$ (Li and Xie 2006). The stream water originates from Mt. Leigu, which has the highest altitude of 4154 m, and flows through the vegetations of heath and meadow ($> 3400 \text{ m}$), spruce-fir forest (3000 ~ 3400 m), mixed broadleaf-conifer forest (2500 ~ 3000 m) and broadleaf forest ($< 2500 \text{ m}$) with the decreasing altitude (Wang 2016). The information of dominant plant species in those vegetations along the altitude is listed in Table S1. The lakes and shoals are distributed in low mountain valleys.

The Guan'egou watershed is one of many ecological hotspot areas around the QTP in China, where the mountain ecosystems generally sensitively respond to climate change (Meng and Liu 2013, 2016; Zhang et al. 2010). Especially, distinct altitude gradient and associated vegetation succession in the study watershed provide a natural experiment for exploring the variations of water evaporation losses with the changing climate and vegetation.

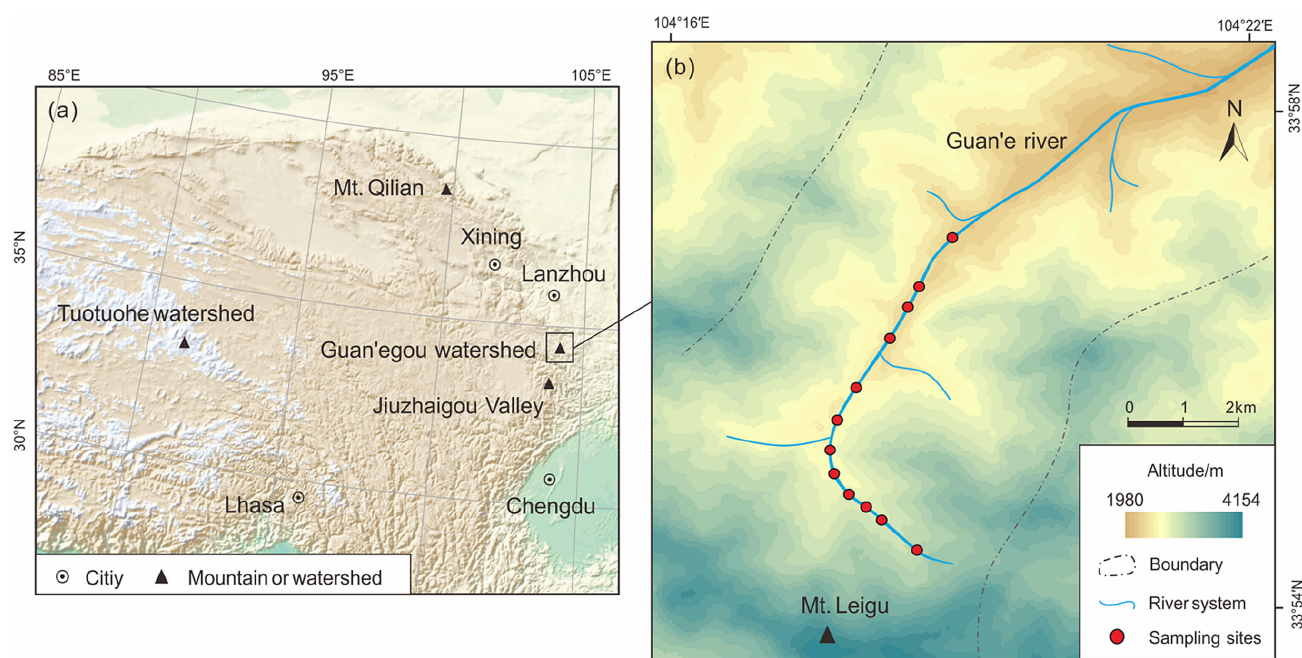


Fig. 1 Location of Guan'egou watershed and sampling sites of stream water

2.2 Stream water sampling and isotope analyses

In September of 2018, stream water was sampled at twelve sites with different altitudes from the north slope of Mt. Leigu (3380 m) to the downstream (2130 m). In each site, the stream water was slowly filled into the glass head-space vials crimp-sealed with butyl septa (W224110-185, Wheaton, USA). The sample vials were taken back to the laboratory in a cooling bag and preserved at 4 °C till laboratory analyses. Water temperature, pH, electrical conductivity (EC), and concentrations of dissolved oxygen (DO) of stream water were measured in the field by using a multiparameter water quality monitor (YSI professional plus, Xylem, USA). The geographic information of longitude, latitude, and altitude was recorded by a GPS at each site. The air temperature at each site was estimated by mean air temperature on the sampling day in Tanchang county (16 °C at the altitude of 1750 m, cited from China Meteorological Data Service Center (<http://data.cma.cn>), and the local vertical lapse rate of air temperature (0.53 °C/100 m) (Li and Xie 2006).

Stream water was transferred and filled up into vials (1.5 mL) in the laboratory before isotopes analyses. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of stream water were analyzed by using the method of high-temperature pyrolysis, and element analyzer coupled with a gas stable isotope mass spectrometer (Flash 2000HT-MAT 253, Thermo Scientific GmbH, Germany) (Gehre and Strauch 2003). Briefly, the water samples were pyrolyzed to H_2 and CO with the presence of reactive carbon at a high temperature

(> 1400 °C) in the element analyzer, then their isotopic compositions ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ values) were measured in the gas stable isotope mass spectrometer after gas chromatographic separation in a constant temperature. Water stable isotopes were then expressed as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (‰) (Clark and Fritz 1997).

$$\delta^2\text{H} = \left[\left(^2\text{H}/^1\text{H} \right)_{\text{sample}} / \left(^2\text{H}/^1\text{H} \right)_{\text{standard}} - 1 \right] \times 1000, \quad (1)$$

$$\delta^{18}\text{O} = \left[\left(^{18}\text{O}/^{16}\text{O} \right)_{\text{sample}} / \left(^{18}\text{O}/^{16}\text{O} \right)_{\text{standard}} - 1 \right] \times 1000, \quad (2)$$

where the Vienna Standard Mean Ocean Water (V-SMOW) is used as the standard. Water isotope standards of GBW04458 ($\delta^2\text{H} = -1.7$ ‰, $\delta^{18}\text{O} = -0.15$ ‰), GBW04459 ($\delta^2\text{H} = -63.4$ ‰, $\delta^{18}\text{O} = -8.61$ ‰), and GBW04460 ($\delta^2\text{H} = -144.0$ ‰, $\delta^{18}\text{O} = -19.13$ ‰) were measured in the same way as stream water samples for data calibrations. Analytical precisions of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were ± 0.5 ‰ and ± 0.2 ‰ based on triplicate sample analyses, respectively. Then, the *d-excess* values were calculated as following (Dansgaard 1964):

$$d - excess = \delta^2\text{H} - 8\delta^{18}\text{O}, \quad (3)$$

the uncertainties of calculated *d-excess* values were ± 0.3 ‰.

3 Results

The $\delta^2\text{H}$, $\delta^{18}\text{O}$, and *d-excess* values of stream water in the Guan'egou watershed ranged from -66.9‰ to -77.1‰ (mean $\pm$ SD = $-69.6\text{‰} \pm 2.6\text{‰}$), -11.4‰ to -10.3‰ (mean $\pm$ SD = $-10.7\text{‰} \pm 0.3\text{‰}$), and 13.5‰ to 18.1‰ (mean $\pm$ SD = $16.0\text{‰} \pm 1.4\text{‰}$), respectively (Fig. 2). The stream water line (SWL) was defined as the linear regression that fitted between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of stream water ($\delta^2\text{H} = 7.65\delta^{18}\text{O} + 12.28$, $N = 12$, $R^2 = 0.72$). Both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of stream water increased with decreasing altitude and increasing air temperature in the study watershed (Fig. 3a, b), showing the enrichment rates of $0.61\text{‰}/100\text{ m}$ and $0.07\text{‰}/100\text{ m}$, respectively.

4 Discussion

4.1 Recharge source of stream water

Because isotopic signatures of surface water basically follow those of precipitation (Meng and Liu 2013, 2016;

Ren et al. 2017), the meteoric water line (MWL) that fitted by $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values can trace the recharge source of surface waters (Kong et al. 2019). The study watershed is located at the transition area of the east edge of the QTP, the Loess Plateau, and Qinling mountains in China (Fig. 1a) (Wang 2016). So far, isotopic surveys of precipitation in and near the study watershed remain very limited. The Jiuzhaigou Valley is geographically closest to our study watershed and has a very similar altitude range (2000–4000 m) (Fig. 1b). The similarity in the climate and landform provides a good opportunity for comparison of precipitation isotopes between these two mountain watersheds (Yin et al. 2000). Therefore, the similar slope and intercept values between the SWL of the study watershed with the MWL ($\delta^2\text{H} = 7.86\delta^{18}\text{O} + 15.07$; $N = 22$, $R^2 = 0.98$) of Jiuzhaigou Valley obtained in September indicated that the stream water in the study watershed was mainly recharged by precipitation at the same period (Fig. 2) (Meng and Liu 2013, 2016; Yin et al. 2000; Wu et al. 2019a).

Because precipitation *d-excess* values can indicate recycled moisture, precipitation derived from arid inland moisture generally had higher *d-excess* values than that

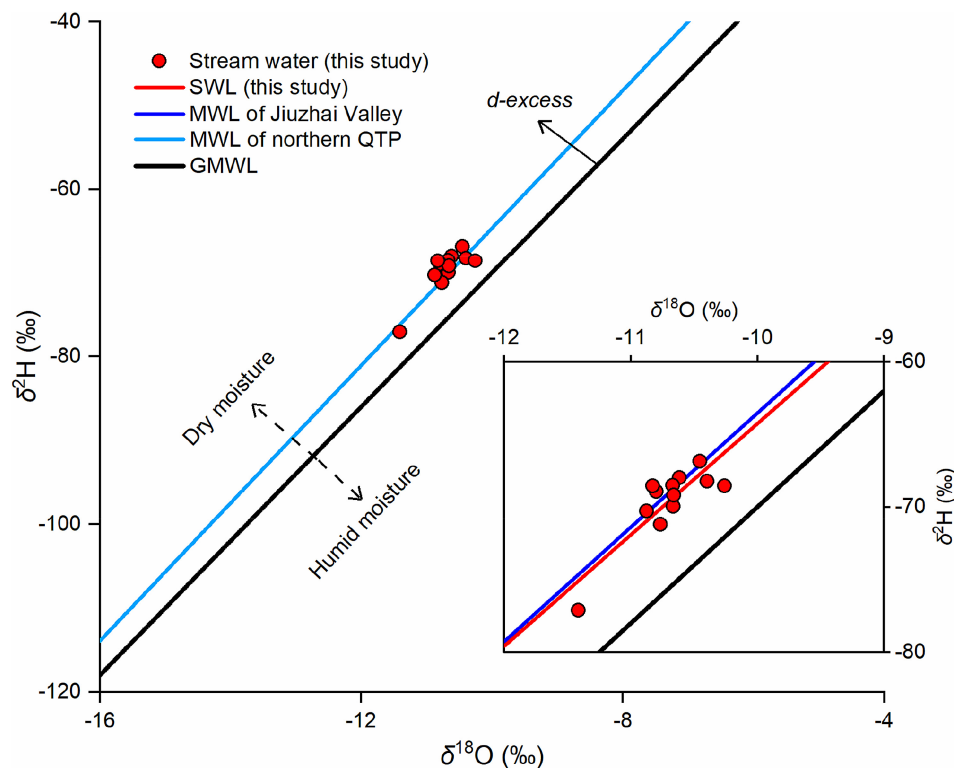
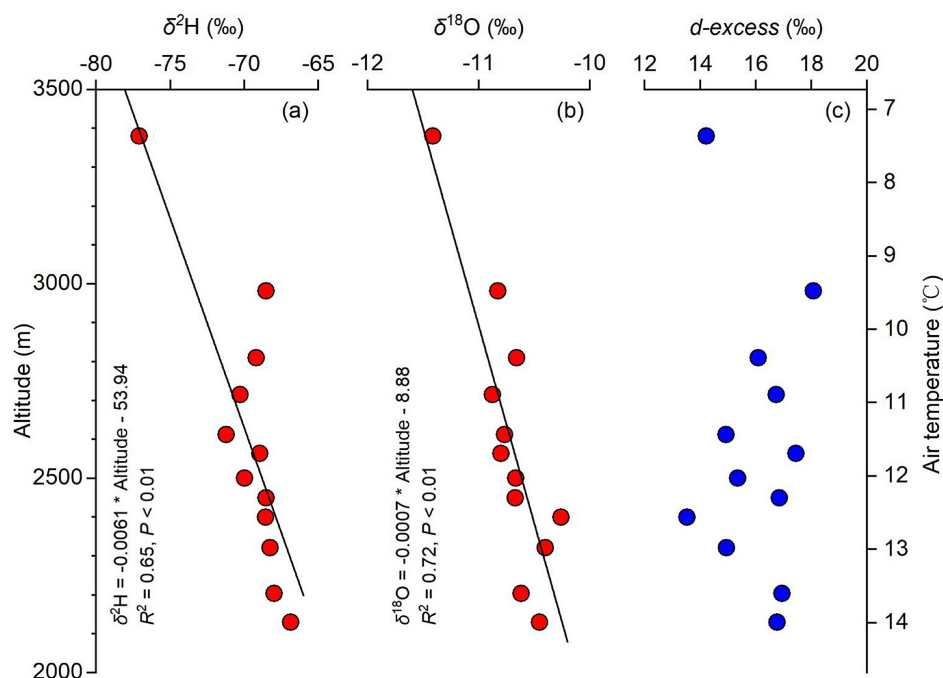


Fig. 2 Distributions of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of stream water in Guan'egou watershed, and a comparison of stream water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values with the meteoric water line (MWL) of northern Qinghai-Tibet Plateau (QTP). The stream water line (SWL) in the Guan'egou watershed ($\delta^2\text{H} = 7.65\delta^{18}\text{O} + 12.28$; $N = 12$, $R^2 = 0.72$) and meteoric water line (MWL) of Jiuzhaigou Valley in September ($\delta^2\text{H} = 7.86\delta^{18}\text{O} + 15.07$; $N = 22$, $R^2 = 0.98$) (Yin et al. 2000) were showed and compared; the MWL of northern QTP was represented by local MWL that obtained in Tuotuohe area ($\delta^2\text{H} = 7.86\delta^{18}\text{O} + 15.07$; $N = 22$, $R^2 = 0.98$) (Tian et al. 2001b); Different deviations of MWLs from the GMWL represent a dry or humid moisture source (dashed arrows); solid arrow represents the increasing trend of *d-excess* values

Fig. 3 Variations of $\delta^2\text{H}$ (a), $\delta^{18}\text{O}$ (b) and $d\text{-excess}$ (c) values of stream water with the altitude (H) and the estimated air temperature (T) in the Guan'egou watershed



derived from warm and humid marine moisture (Froehlich et al. 2008; Li et al. 2015; Liu et al. 2007; Tian et al. 2001b), which causes deviations of isotopic distributions from the GMWL (Fig. 2). Especially, in the Qinghai-Tibet Plateau (QTP), higher $d\text{-excess}$ values of precipitation in northern areas were mainly attributed to the dominance of inland moisture, rather than the marine monsoon (He and Richards 2016; Liu et al. 2007; Tian et al. 2001a; Zhou et al. 2007). Therefore, the differences of observed $\delta^2\text{H}$ and $\delta^{18}\text{O}$ distributions of stream water from the GMWL might exclude the dominance of marine monsoon moisture in precipitation (Liu et al. 2007, 2010; McGuire and McDonnell 2007) (Fig. 2). Similar isotopic distributions of stream water in our study watershed with the precipitation in northern QTP areas such as the Tuotuohe area revealed that the inland moisture from the continental monsoon or local recycled vapor at the end of the rainy season (Tian et al. 2001a, 2001b) (Fig. 2; Fig. S1). These results highlighted an effective diagnose of the moisture source of precipitation in semi-arid areas by combining distributions of water isotopes with the $d\text{-excess}$ values (Kong et al. 2019; Li et al. 2020; Pfahl and Sodemann 2014; Tian et al. 2007).

4.2 Estimation of water evaporation losses of stream water

Both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of stream water in the study watershed showed distinct altitude effects (Hren et al. 2009; Ren et al. 2017). However, the observed lapse rates of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values with increasing altitude were lower

than those of surface water flows in the QTP (Ren et al. 2017; Wen et al. 2012; Wu et al. 2019a; Yang et al. 2009). Such differences were mainly caused by the low precipitation at the end of the rainy season (Fig. S1) when the mixing of different moisture sources might have generated the altitude decoupling of air mass and terrains (Wen et al. 2012; Yang et al. 2009; Yao et al. 2013). Previously, the evaporation has been found to enhance the altitude effect of river $\delta^{18}\text{O}$ values at regional scales but has often been neglected at watershed scales (Wu et al. 2019a; Yang et al. 2009). In our study watershed, however, the water evaporation losses played an important role in regulating the variations of stream water isotopes with the altitude (Wu et al. 2019b).

Because stream water isotopes were controlled by isotopic compositions of precipitation and evaporation isotope effects, the altitude effects of stream water isotopes could reflect water distillation processes (Edwards et al. 2015; Wu et al. 2019a, 2019b). Assuming a transient equilibrium state of the water–vapor interface during the evaporation, the fractionation factor could be only related to temperature (Skrzypek et al. 2015; Wassenaar et al. 2011). In another word, we aimed to estimate the water losses of the equilibrium evaporation processes to reflect their variations along the altitude gradient. While the kinetic fractionation of ^2H is larger than that of ^{18}O in evaporation, the $\delta^{18}\text{O}$ value of stream water is better to estimate the equilibrium water evaporation losses (Luz et al. 2009). The $\delta^{18}\text{O}$ values of stream water at the highest altitude (denoted as H_0 , where the temperature is T_0) and lower altitudes (denoted as H_n , where the temperature is T_n) can be considered as

those of initial and residual water. Accordingly, each water equilibrium evaporation process could be described as the following open-system Rayleigh equation (Wassenaar et al. 2011) (Eq. 4).

$$\delta^{18}\text{O}_n + 1 = (\delta^{18}\text{O}_0 + 1) \times (1 - E_n)^{(\alpha_n - 1)}, \quad (4)$$

where $\delta^{18}\text{O}_0$ and $\delta^{18}\text{O}_n$ values are $\delta^{18}\text{O}$ values of stream water at the altitude of H_0 and H_n , respectively. The E_n is the fraction of water evaporation losses (%). The α_n is the equilibrium isotope fractionation factor and was estimated by the following equation (Clark and Fritz 1997; Gat 1996; Majoube 1971).

$$10^3 \ln \alpha_n(^{18}\text{O}) \approx (1.137 \times 10^6) / T_e^2 - 415.6 / T_e - 2.0667, \quad (5)$$

where T_e is the air temperature (in Kelvin) of the water–vapor interface and is estimated as the mean air temperature between the altitudes of H_n and H_0 .

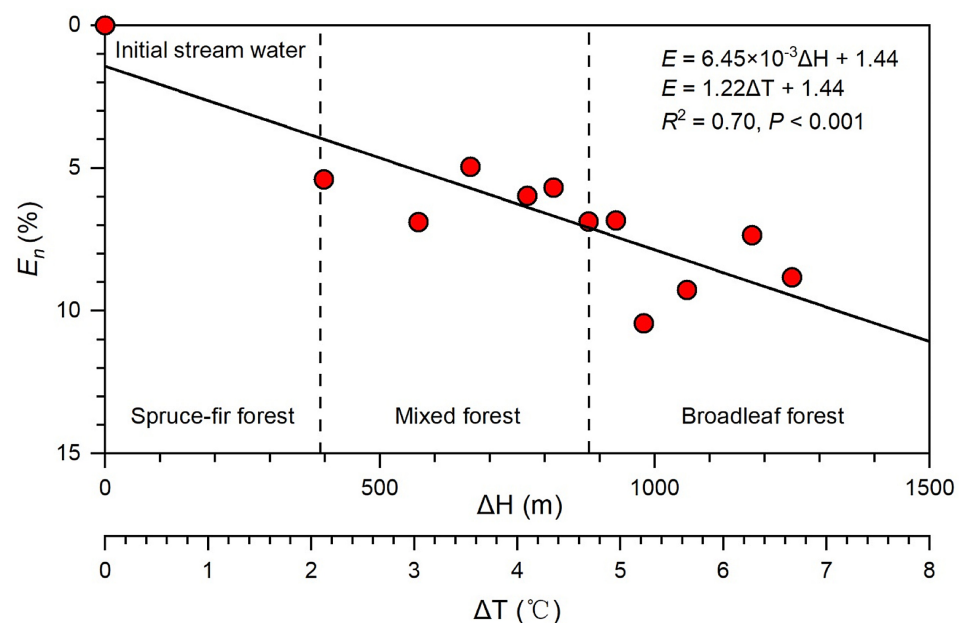
The calculated E_n values based on Eq. 4 ranged between 4.97%–10.44%, reflecting distinct vertical differences of water evaporation losses in the study watershed (Kong et al. 2019; Wu et al. 2019a). Moreover, the E_n values increased with the altitude lapses ($\Delta H_n = H_0 - H_n$) and the temperature increments ($\Delta T_n = T_n - T_0$) ($P < 0.01$; Fig. 4). This revealed the importance of temperature variations for shaping the heterogeneity of hydrological processes in mountain ecosystems (Guo et al. 2016; Yao et al. 2013). The calculating results and findings are useful for water budget estimations in mountain areas, which should be integrated into water balance models (Fan et al. 2019; Jasechko et al. 2013).

The vegetation is a key factor affecting water evaporation losses at the landscape scale (Jiang et al. 2004). We found that the increments of E_n values differed with the vegetation (Fig. 4; Table S1), water evaporation losses showed a mean rate of 1.36%/100 m in the subalpine spruce–fir forest at the upper mountain, 0.31%/100 m in the mixed broadleaf–conifer forest at the middle mountain, 0.61%/100 m in the broadleaf forest at the lower mountain. Although the equilibrium evaporation that dominated by temperature was partly hypothetical, the result reflected the differences of vegetation in restricting soil water evaporation potentially due to different litter compositions and tree canopy sizes (Edwards et al. 2015; Jiang et al. 2004). Among vegetations along the altitude gradient, the higher plant diversity in the broadleaf forest and mixed broadleaf–conifer forest than that in the spruce–fir forest could also promote soil water retention (Table S1) (Kammer et al. 2013; Sundqvist et al. 2013; Wu et al. 2014). Meanwhile, water evaporation losses can affect the vegetation succession by altering local precipitation (Zhang et al. 2010). Our results highlighted that vegetation and hydrological processes can interact in influencing the structure and function of mountain ecosystems.

5 Conclusions

Stable isotopes and *d-excess* values of stream water in a mountain watershed around the QTP revealed precipitation dominated by inland moisture from the continents or local water vapor as the main recharge source. Stable isotopes of stream water increased distinctly with decreasing altitudes,

Fig. 4 Variations of water evaporation losses (E_n) with the altitude lapses (ΔH) and temperature increments (ΔT) of stream water in the Guan'egou watershed. The red-filled circles represented the water evaporation losses (E_n) in different altitude lapses (ΔH) and temperature increments (ΔT); the initial stream water ($E_0 = 0$, $\Delta H = 0$, $\Delta T = 0$) was showed; the dashed lines represented the boundaries of vegetations at different altitudes; The mixed forest is the abbreviation of the broadleaf–conifer forest



which indicated the variations of water evaporation losses along the altitudes. A Rayleigh isotope model based on water $\delta^{18}\text{O}$ values was established to estimate the fractions of water evaporation losses, which increased with the decreasing altitude and increasing temperature. Moreover, the increments of fraction values differed among vegetation types. This study provided useful hydrogeochemical information of surface waters in mountain watersheds to better understand relationships between hydrological processes, climate, and vegetation surrounding the QTP region.

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Compliance with ethical standards

Conflict of interest We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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