Water Policy 21 (2019) 368–381

Stable isotope tracers as diagnostic tools in studying water sources in a humid bamboo watershed during the plum rainfall events

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Abstract

This study investigates the temporal variation of stable isotopic composition in precipitation, soil water, and streamflow water during the plum rainfall events in an upland headwater watershed which is mainly covered with bamboo. The results show that the isotopic composition of various water sources exhibit significant temporal variation. The local meteoric water line is established by using the relationship between the stable isotope of oxygen-18 and deuterium, which is slightly different from the meteoric water line of China. The isotopic temporal variation of precipitation is closely related to exchange effect between raindrops and environmental vapor, evaporation fractionation and rainfall intensity. The isotopic variation of shallow soil water is mainly determined by canopy interception, ground evaporation and the mixing with pre-event water; as for the isotopic variation of deep soil water, it is virtually influenced by pre-event water. The most enriched isotopic composition of streamflow and deuterium excess (d-excess) differences between streamflow and rainfall both indicate that streamflow is recharged not only by event water but also by pre-event water. Hence, a better understanding of precipitation formation and the hydrological response under the plum rainfall system may be instructive for the management of water resources in humid watersheds in southern China.

Keywords: Hemuqiao watershed; Precipitation; Soil water; Stable isotope; Streamflow water

Introduction

Monsoons are defined as prevailing wind directions on a large scale which change significantly with distinct seasonal precipitation and last for a long period. The major monsoon systems on the global scale include the Asia–Australia, the African, and the America monsoons which depend on the temperature difference between the ocean and the continent. China is situated in the region of the East Asian monsoon whose climatic characteristic is clear seasonality. In particular, water resources

doi: 10.2166/wp.2019.137

in eastern China mainly come from precipitation carried by monsoon. The summer precipitation between May and September accounts for about 70% of annual precipitation. It plays an important role in economic development and agriculture production. The East Asian monsoon abnormal behaviors influenced by El Niño and La Nina cause extreme droughts and floods (Torrence & Webster, 2010; Ummenhofer *et al*., 2011). A typical type of precipitation which occurs on the interface between a warm front and cold front is called plum rainfall. The westerlies weaken significantly with the increasing intensity of the East Asian monsoon, and the rainbelt stretching for thousands of kilometers moves northward. The distribution of the plum rainfall is a significant influencing factor of floods and droughts in the Yangtze River and Huaihe Basin (Zhu *et al*., 2016). Hence, a better understanding of the precipitation process and the hydrological response under the plum rainfall system may be instructive for the management of water resources and the prediction of disasters in southern China.

In the global water circulation system, the water body undergoes a series of processes such as evaporation, condensation, infiltration, and runoff (Gat, 2003). The stable isotope tracer of the water body is sensitive to the variation of the environmental condition. This characteristic means the stable isotope becomes a useful diagnostic tool for many studies such as hydrology (Vitvar *et al*., 2002; Farrick & Branfireun, 2015), paleoclimatology (Jiang & Zhi-Zhong, 2010), and ecology (Chamberlain *et al*., 1997; Radajewski *et al*., 2000). Precipitation is an important component of water circulation at the global scale, and the stable isotopic (δD and δ^{18}O) composition of it is influenced by the processes of moisture generation (Aggarwal *et al*., 2004), moisture transport (Irving *et al*., 2002; Sinclair *et al*., 2011), and atmospheric circulation (Jouzel *et al*., 1997). For small basins, the local climate and geographical environment conditions also modify the stable isotopic composition in precipitation (Allen *et al*., 2015; Gu *et al*., 2018). Generally speaking, the factors affecting the temporal and spatial variation of isotopic value mainly include amount effect (Yu *et al*., 2007), temperature effect (Vimeux *et al*., 2005), altitude effect, and latitude effect (Field *et al*., 2010).

Stable isotopes (δ^2H and δ^{18}O) provide additional information about the water source, flowpath and age at the hillslope and headwater catchments, which is very important in order to deepen our understanding about the physical mechanisms of runoff generation (Bonell, 1993; McGuire *et al*., 2002; Monteith *et al*., 2010). Many hydrological studies have explored the temporal and spatial variation in isotopic composition of various water sources, such as precipitation (Price *et al*., 2008), streamflow (McDonnell *et al*., 1991), soil water (Tsujimura, 1998), and groundwater (Govender *et al*., 2015) to separate the storm hydrograph at the outlet of the watershed. Isotopic hydrograph separation analysis can avoid the subjectivity and arbitrariness of graphical hydrograph separation (Lin *et al*., 1997; Klaus & McDonnell, 2013).

There are few studies using stable isotopes to explore the various water sources responses during the plum events in humid bamboo watersheds. Our specific purposes are: (1) study the relationship between the stable isotopes δ^2H and δ^{18}O of precipitation in Hemuqiao watershed and establish the local meteoric water line (LMWL) during the plum rainfall events; (2) explore the main factors influencing the temporal variation in isotopic composition of precipitation, shallow layer soil water, deep soil water, and streamflow; (3) evaluate the runoff generation mechanism by using the deuterium excess (d-excess) differences between streamflow water and precipitation.

Study area

Hemuqiao watershed (30°34′N–119°47′E) is located within the upstream of Jiangwan basin, 50 km west of Hangzhou, China (Figure 1). The drainage basin area is 1.35 km^2 and the elevation is approximately 150–600 m above sea level. The study watershed belongs to the subtropical monsoon climate with a mild winter and a cool summer. Mean annual temperature is about 14°C, the highest temperature in July is 25°C, and the lowest temperature in January is 1.3°C. Average annual precipitation is 1,580 mm and most of it occurs from May to October. The average annual water surface evaporation is about 805 mm.

The watershed is mainly covered with bamboo (90%) and the remainder with potato, tea, and other crops. Along the river channel is a cement road from the upstream to the outlet of the study watershed.

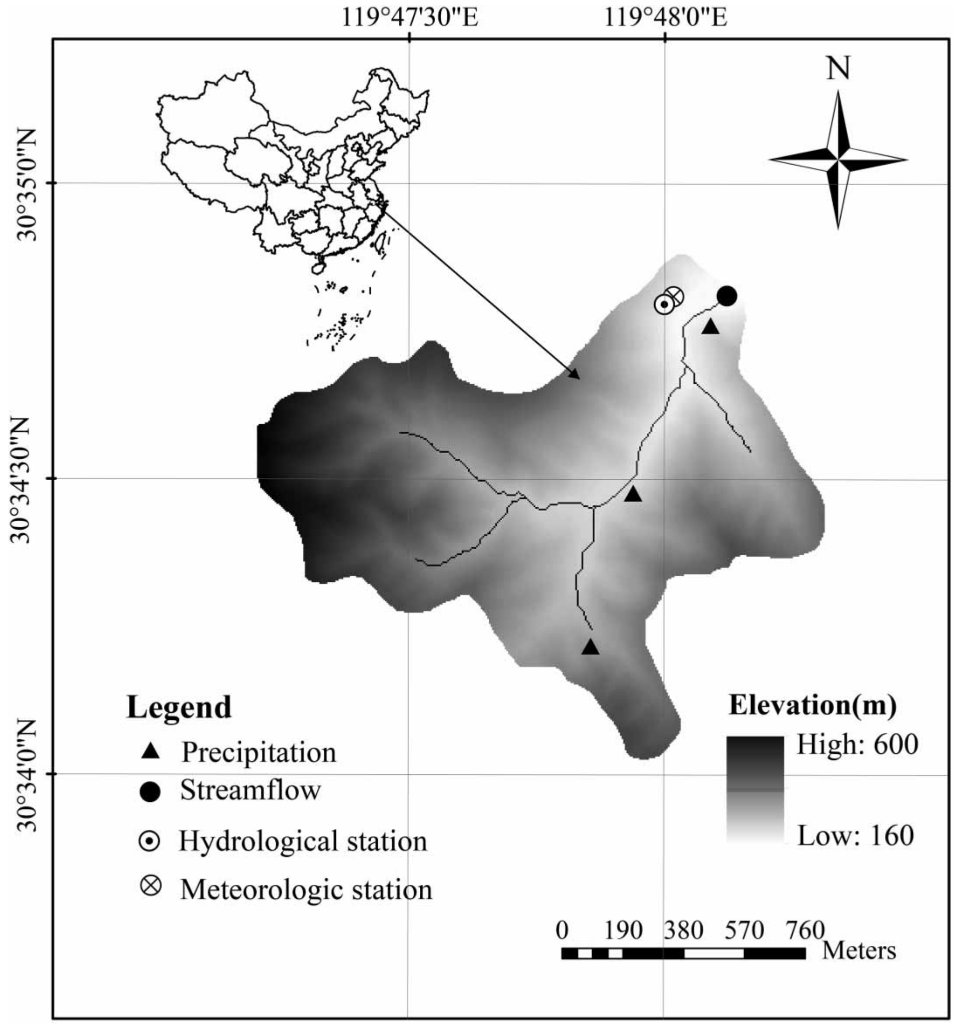

Fig. 1. Location of Hemuqiao watershed and sampling points.

The road is mainly used to transport bamboo in order to promote regional economic prosperity and to improve living standards. The average slope of Hemuqiao watershed is between 25° and 45°, and the slope in the upstream is larger than that of downstream. The main type of bedrock in this area is Late Mesozoic igneous rock, and near the channel is mainly covered by weathered Late Mesozoic igneous rock. The soil type in the study area includes sandstone and siltstone and soil depths range from 1.5 to 2.5 m. The properties of the soil and bedrock lead to the high infiltration rate (average 43.0 cm/h), and vertical distribution determines the infiltration rate varies with the depth (Liu *et al.*, 2016). For a study area with high permeability and large slope, it is difficult to generate surface storage. In addition, the influence of human activities on this watershed have been overlooked.

Methods

There are many devices installed in the Hemuqiao watershed in order to collect hydrological data. The discharge of the watershed outlet is measured by a 90° sharp crested V-notch. The pressure of atmospheric and river bottom are measured simultaneously every 6 minutes. Subsequently, the pressure signal was converted into electrical signals and stored in the logging devices. The water level is calculated by the pressure differences between atmospheric and river bottom. Discharge is calculated by the relationship of stage–discharge and the relationship is established before rainfall events. The tipping-bucket rain recorder installed in the upstream is used to measure rainfall. There is a meteorological monitoring station at the outlet of the watershed which provides long-term monitoring of temperature, solar radiation, wind speed, wind direction, and near surface humidity data.

The experiment was conducted between June and July in 2017, and during this period two plum rain events occurred. Bulk samples of plum rain were collected during each event with a polyethylene barrel installed in the open area of upstream, middle reach, and downstream, respectively. Bulk samples of throughfall were collected with the same barrels, which were installed under the bamboo with medium canopy in the upstream, middle reach, and downstream of the watershed, respectively. The diameter and the height of polyethylene barrels are 50 cm. In order to study the temporal variation of throughfall and rainfall isotopic composition, hourly samples were collected in the middle reach of the watershed from 8:00 am to 18:00 pm during the plum rain events. We did not collect rainfall and throughfall samples during the night-time and the isotopic data at 8:00 am next day was used to represent the weighted average of the isotopic composition of night precipitation. The streamflow water was collected by artificial sampling at the outlet of the watershed from 8:00 am to 18:00 pm hourly. All water samples were sealed and stored in 30 mL polyethylene sampling bottles in order to prevent evaporation fractionation. The sampling bottles were labeled with the collecting time and water sample type. The samples were stored in the refrigerator at 4°C until analysis. Soil samples were collected at a depth of 10 cm and 100 cm, respectively. Soil samples were collected by shovel every 2 hours during the plum rainfall events, and sealed in the polyethylene storage bag to avoid evaporation. Soil water was extracted from soil samples by distillation for isotopic analysis after being taken back to the laboratory.

The isotopic compositions of all samples were analyzed by Thermo Fisher MAT253 in the State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering in Hohai University. Each sample was analyzed four times, including stable isotope oxygen and hydrogen. The first two results were deleted to eliminate the memory effect of the machine, and the last two results averaged to represent the isotopic composition of the sample. The isotopic compositions of hydrogen and oxygen are expressed as δ (per mil) of samples relative to the laboratory standards, subsequently normalizing the hydrogen and oxygen isotope data to the scale of Vienna Standard Mean Ocean Water. The precision of the δ^{18}O and δ^2H measurements weree ± 0.2‰ and ± 2‰, respectively.

Results and discussion

Local meteoric water line

Craig (1961) defined the stable isotope relationship between δ^{18}O and δ^2H in precipitation of global scale as the global meteoric water line (GMWL). It is of great significance for studying the global hydrological cycle. On the global scale, the GMWL is expressed as: $\delta^2H = 8\delta^{18}O + 10$. The gradient of the GMWL indicates the ratio of hydrogen and oxygen isotope fractionation rates and the ordinate intercept represents the deviation between the real state and equilibrium state. Generally speaking, different regions have a different meteoric water line which is defined as the local meteoric water line (LMWL). That is mainly due to differences in temperature and humidity in the condition of water vapor generation, fractionation during the water vapor migration from ocean to continent, and exchange effect between falling raindrops and ambient moisture (Gat, 2003). The LMWL plays an important role in studying the migration of water vapor, local physical geography, and weather conditions (Gat, 2003).

In this study, the least square method is used to calculate the relationship between the stable isotopes of δ^{18}O and δ^2H during the plum rain events. The linear fitting equation is expressed as: $\delta^2H = 7.78\delta^{18}O + 4.85$ ($R^2 = 0.9775$) (Figure 2). The slope of this equation is 7.78 which is less than that of the GMWL. The smaller slope indicates the role of evaporation effect and exchange with ambient moisture while the raindrops fall down from the cloud to the watershed.

At the beginning of plum rainfall events, the high temperature and low humidity environment cause high evaporation effect. With the progress of precipitation events, the exchange effect may be the main

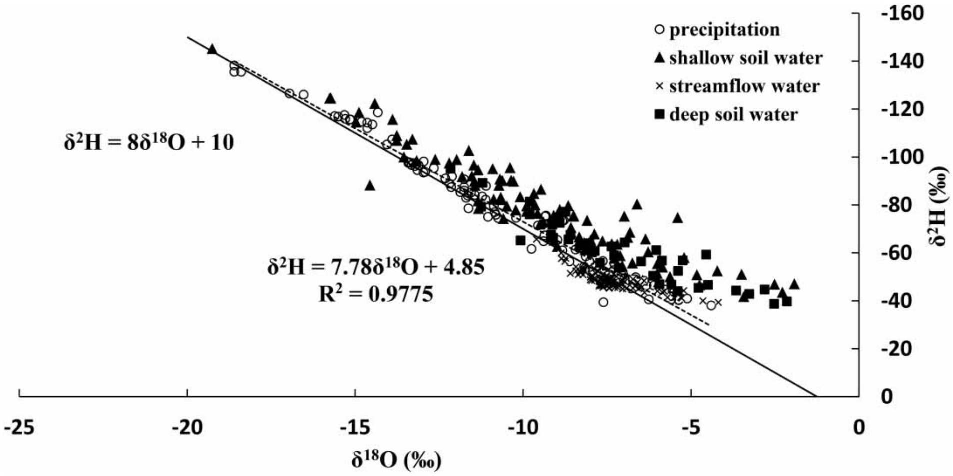

Fig. 2. All δ^{18}O and δ^2H data during the plum rain events of precipitation, shallow soil water, streamflow water, and deep soil water relative to the local and global meteoric water lines. The LMWL is calculated from precipitation samples. The black line represents the GMWL, and the dotted line represents the LMWL. *Note:* R^2 is the coefficient of determination.

factor influencing the value of stable isotopes in the high humidity environment. The ordinate intercept of LMWL is 4.85 which is less than that of the GMWL. The slope and the ordinate intercept of the LMWL are determined by different influencing factors. The intercept is mainly related to the evaporation conditions of the water vapor source, including salinity of sea water, ocean surface temperature, wind speed, air pressure, and the most important factor is ocean surface humidity. When the ocean surface humidity is 100%, the isotopic composition of water vapor and seawater are under the equilibrium condition, and the ordinate intercept is 0. When the ocean surface humidity is about 85%, the ordinate intercept is close to 10. The ordinate intercept of 4.85 during the plum rainfall events indicates that the ocean surface humidity is between 85% and 100%.

Zheng *et al.* (1994) fitted the meteoric water line of China by analyzing the monthly isotopic composition of precipitation collected from eight stations in China during 1980. The linear fitting equation is expressed as: $\delta 2\mathrm{H} = 7.9\delta^{18}\mathrm{O} + 8.2$ ($n = 101$). The LMWL during the plum rainfall events in Hemuqiao watershed is slightly different from the meteoric water line of China. This might partly be because monthly atmospheric precipitation includes various rainfall types, such as orographic rain, thundershower, convectional rain, and snowfall. However, the LMWL of Hemuqiao watershed was established from the stable isotope of hourly atmospheric precipitation during the plum rainfall events. The different types of rainfall events may have different formation conditions and migration times of water vapor. Hence, the gradient and intercept of the two atmospheric water lines are different.

Isotopic composition variation in different water sources

Isotopes of precipitation. Generally speaking, the variation range of rainfall isotopic composition during the plum rain events in Hemuqiao watershed is in the variation range of rainfall isotopic composition of precipitation in China (Wang *et al.*, 2013). The arithmetic mean values of two plum rainfall events are −10.97‰ and −9.90‰ for δ^{18}O, −82.10‰ and −73.80‰ for δ^{2}H, respectively. The δ^{18}O and δ^{2}H values during the plum rainfall events exhibit significant changes. This is mainly related to the characteristics of rainfall events mainly affected by the frontal structures.

During the middle 10 days of June, the northwest wind gradually weakened with the strengthening Indian monsoon and Pacific monsoon. A warm and humid marine air parcel moved across the coast into the continent, and then moved northward. A great deal of water vapor is brought into the continent by the summer monsoon from the ocean. Due to the temperature differences between the cold front and warm front, the densities of these fronts are different, and the cold front is always wedged under the warm front. Marine moisture climbs along the cold front slowly and then the temperature of marine moisture falls. Because there are obvious differences between the cold and warm fronts in meteorological elements such as temperature, humidity, and pressure, precipitation will occur near the front. The unstable front system leads to a significant change in rainfall intensity, total precipitation, and duration.

Figure 3 represents the δ^{18}O value variation of rainfall during storm 1. Study of the main factors affecting the variation in isotopic composition of precipitation should be based on the characteristics of the plum rainfall events.

At the beginning of the rainfall event, the isotopic value of δ^{18}O is relatively depleted. Subsequently, the isotopic value of δ^{18}O exhibits a rapid increase. At this stage, the main factor affecting the variation in δ^{18}O of precipitation is exchange effect. The characteristics of water vapor in the front of the cold frontal area are cold and dry, mainly due to re-evaporation effect on the land. The isotopic composition of water vapor produced from an inland hydrological cycle is more depleted than that carried by summer

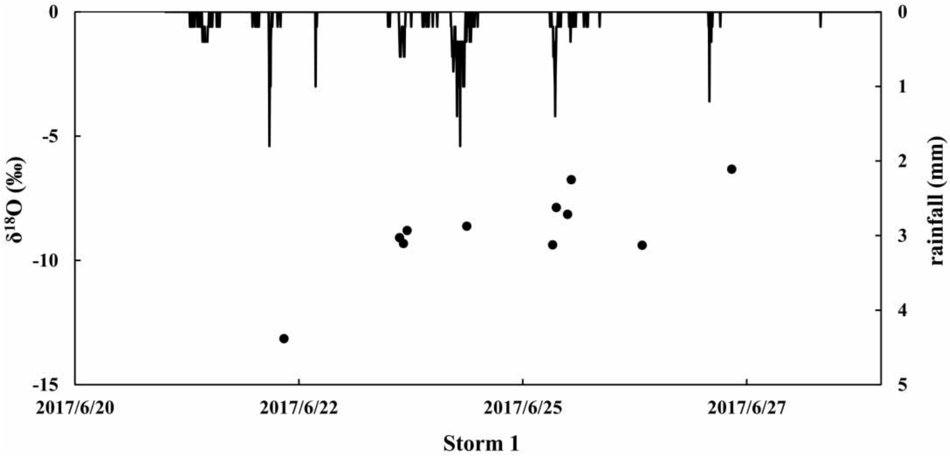

Fig. 3. Variation of $\delta^{18}O$ values in precipitation during storm 1 in Hemuqiao watershed.

monsoon. During the plum rainfall events, the falling raindrops enter the cold frontal area and the isotopic composition of the raindrops is modified by exchange with more depleted environmental water vapor. Afterwards, the isotopic composition of ambient water vapor is close to that of raindrops. The effect of exchange between raindrops and ambient water vapor becomes gradually unremarkable, and then the isotopic composition of precipitation shows a slightly increasing trend between 17:00 pm on July 23 and 9:00 am next day.

With the progress of precipitation, the isotopic value of $\delta^{18}O$ fluctuates between −9.37‰ and −6.75‰ during the period of 9:00 am on July 24 to 8:00 am on July 26. Both evaporation effect and rainfall intensity determine the change of isotopic value of $\delta^{18}O$. The isotopic value of $\delta^{18}O$ is more enriched due to the intense evaporation effect. Nevertheless, there is a strong negative correlation between rain intensity and the isotopic value of $\delta^{18}O$. In the case of low rainfall intensity, the evaporation effect is greater and the isotopic composition of precipitation is gradually enriched, but in contrast, the high rainfall intensity and low evaporation effect makes the isotopic composition of precipitation gradually depleted.

During the last period of the plum rainfall event, the isotopic value of $\delta^{18}O$ exhibits an increasing trend. The intensive re-evaporation and exchange effect may be the main factors leading to greater enrichment of the isotopic value of precipitation. The water in the watershed returns to the air due to re-evaporation effect under the rising temperature in the short non-rain period during the plum rainfall events. The isotopic composition of ambient vapor in the current period is probably more enriched than that of ambient vapor before the plum rainfall event. The humidity in the current period may be also higher than that in the beginning of the rainfall event. The exchange effect between falling raindrops and ambient vapor with high humidity and enriched heavy isotope becomes more significant. Hence, the isotopic value of $\delta^{18}O$ during the last period of rainfall event is more enriched.

Figure 4 depicts the variation of isotopic value of $\delta^{18}O$ during storm 2. At the beginning of the rainfall event, the isotopic value of $\delta^{18}O$ exhibits a similar increase trend as storm 1. At this stage, the main factor affecting the variation of $\delta^{18}O$ in precipitation is exchange with depleted environmental vapor, too. With the process of rainfall event, the isotopic value environmental vapor increases which makes the isotopic value of rainfall exhibit a similar increasing trend. However, the isotopic value of

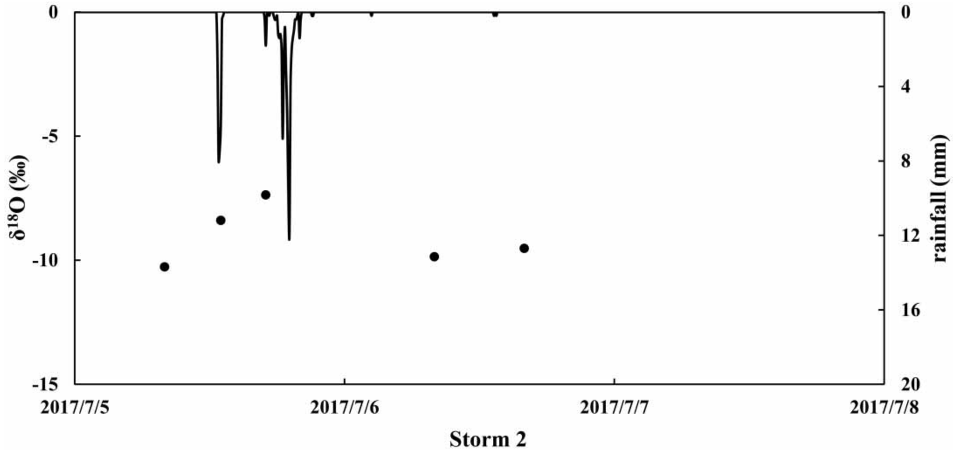

Fig. 4. Variation of δ^{18}O value in precipitation during storm 2 in Hemuqiao watershed.

δ^{18}O exhibits an increasing trend in the last period of the plum rainfall event which is different from storm 1. Rainfall intensity may be the main factor influencing the variation of isotopic value of δ^{18}O and the evaporation effect can be ignored. During 18:00–20:00 on July 5 (2017), heavy rainfall intensity (average 28.7 mm/h) of short duration occurred in the study area with low temperature and high relative humidity. Under this condition, the non-equilibrium evaporation hardly influences the isotopic composition of falling raindrops and the surface storage in the watershed.

Isotopes of shallow soil water. The stable isotope δ^{18}O and δ^{2}H values of shallow soil water during the plum rainfall events are shown in Table 1. Results show that isotopic composition of shallow soil water is more enriched than that of precipitation during the plum rainfall events. This is mainly due to three factors affecting the variation of δ^{18}O value in shallow soil water:

1. Interception effect by bamboo. There is a significant difference between isotopic composition of precipitation and that of throughfall (Qu *et al.*, 2017). The isotopic value of throughfall is more enriched

Table 1. The statistics of stable isotopic composition of precipitation, shallow soil water, deep soil water, and streamflow water in the plum rainfall events in 2017.

		δ^{18}O (‰)			δ^{2}H (‰)		
Rainfall events	Water source	Max	Min	Arithmetic mean	Max	Min	Arithmetic mean
Storm 1	Precipitation	−5.37	−18.60	−10.97	−40.40	−138.10	−82.10
	Shallow soil water	−1.93	−19.26	−9.58	−41.60	−145.00	−80.50
	Deep soil water	−2.15	−9.81	−7.94	−38.70	−76.00	−54.30
	Streamflow water	−4.19	−9.60	−7.53	−39.30	−65.70	−48.70
Storm 2	Precipitation	−7.37	−10.27	−9.90	−55.00	−78.20	−73.80
	Shallow soil water	−3.50	−13.17	−8.48	−46.50	−98.30	−70.50
	Deep soil water	−4.55	−10.08	−7.84	−55.80	−77.10	−64.80
	Streamflow water	−5.28	−8.21	−7.18	−41.10	−53.50	−48.60

than that of rainfall, which is mainly related to the canopy interception by bamboo. The falling raindrops reach the leaves of bamboo before reaching the ground. Due to the high specific surface area of the bamboo canopy, the storage capacity of the canopy cannot be ignored. At the beginning of the plum rain events, due to the canopy interception effect, most of the falling raindrops with depleted isotopic composition were stored on the bamboo leaves' surface. Subsequently, the following enriched raindrops mix with the depleted precipitation stored on the leaves' surface. Mixing makes the isotope compositions of water on the bamboo leaves' surface more enriched. After the canopy is saturated, excess water drops fall directly to the ground, or reach the ground in the form of stem-flow. At the same time, the high specific surface area means that the water droplets stored on the leaves are in greater contact with the air and the evaporation fractionation effect is more intense. This is another reason why isotopic composition of precipitation is more depleted compared with that of throughfall during precipitation events.

2. The ground evaporation. After raindrops fall on the ground, a proportion of them are intercepted or absorbed by dry forest litter, and the remaining raindrops begin to infiltrate into the soil. Due to the high temperature during rainfall events, the effect of evaporation fractionation cannot be ignored, which also makes the isotopic composition of shallow soil water more enriched than that of precipitation.
3. Mixing with pre-event water. The soil water stored in the watershed before the plum rainfall events plays an important role in the variation of soil water isotopic composition. The pre-event water undergoes long-term evaporation fractionation, and during the initial stages of rainfall events, the raindrops do not infiltrate into the soil immediately, with the result of much enriched isotopic composition of shallow soil water (the arithmetic mean value $\delta^{18}O$ is $-8.43‰$) at the beginning of sampling. With the progress of rainfall events, the great change in isotopic composition of shallow soil water indicates the mixing between infiltrating raindrops and pre-event water. This reveals the response mechanism of shallow soil water to the plum rain events.

Isotopes of deep soil water. The stable isotopic composition of deep soil water is more enriched than that of rainfall and shallow soil water (Table 1). The variation range of deep soil water isotopic composition is relatively small, which might be due to the slight influence of rainfall events and significant influence of storage water stored in the watershed before rainfall events, which is also defined as pre-event water. The streamflow is divided into event water and pre-event water according to water sources, and these components are also known as new water and old water. Soil water and groundwater are the main components of pre-event water. After a long period of evaporation fractionation the pre-event water undergoes a weaker exchange with the surrounding rocks in the process of recharge to the deep layer. Both evaporation and exchange with the surrounding rocks cause the soil water to be isotopically enriched.

At the beginning of precipitation events, after the upper layer of soil water content reaches saturated moisture content, excess water moves downward under the influence of gravity. The mixing between the infiltrated moisture and pre-event water in deep layers makes the isotopic composition of deep soil water more uniform.

Isotopic composition of streamflow water. In general, compared with other water sources, isotopic composition of streamflow water is the most enriched, and the variation range is significantly smallest.

Figure 2 shows the δ^{18}O values of streamflow water are distributed along the LMWL indicating that it seems to be recharged by precipitation. However, the isotopic value in streamflow water concentrated in the lower part of the LMWL indicates that it is recharged not only by rainfall. Only the stable isotopic data in the plum rainfall events were used to establish the LMWL without considering seasonal variation of precipitation. The infiltrated water recharged by different precipitation events undergoing evaporative fractionation and exchange with surrounding rocks gradually mixes well in the soil layer and groundwater. That will lead to the enriched isotopic value of groundwater in the humid watershed. This may provide powerful evidence that the streamflow water in the headwater catchment was mainly recharged by pre-event water.

During the plum rainfall events, there is an obvious change in the proportion of pre-event water. After the plum rainfall events, the discharge of the pre-event proportion rapidly decreases to the initial stage (Gou *et al.*, 2018). This shows that the discharge of pre-event water responds to the plum rainfall events sensitively. The soil layer has large infiltration capacity (average 43.1 cm/h) in Hemuqiao watershed, and the large vertical hydraulic conductivity means the soil water mainly infiltrates into deeper layers under the force of gravity. During the migration process, the event water (usually refers to current precipitation) forces the pre-event water in the vadose zone to flow downwards which makes the discharge of groundwater vary significantly during the plum rainfall events.

Temporal variation of d-excess of precipitation and streamflow water. The differences in slope and intercept between LMWL and GMWL can provide additional information about the vapor sources, a secondary effect in the condensation-evaporation process (Dansgaard, 1964). In order to quantify the difference during the rainfall events, we use the expression $d = \delta^2H\text{-}8\delta^{18}O$ to calculate d-excess. The equilibrium fractionation will not affect the d-excess, nevertheless, d-excess is associated with non-equilibrium fractionation such as evaporation and condensation. When the d-excess value is 10, these data points are distributed along the GMWL indicating samples are undergoing equilibrium fractionation. When the d-excess value is less than 10, these data points' distribution deviate from the GMWL indicating the samples are undergoing evaporation fractionation. Hence, in this study, we use the d-excess value as an indicator of evaporation.

Figure 5 shows the temporal variation of d-excess of the rainfall samples during the period of storm 1 and storm 2. The variation range of d-excess of rainfall is significant and ranges from −8.32‰ to 12.56‰ for storm 1 and 2.76‰ to 10.74‰ for storm 2, respectively. The arithmetic mean value of d-excess is 3.09‰ and the weighted average of that is 3.38‰ for storm 1, and that for storm 2, 6.10‰ and 5.00‰, which is lower than that of the average global meteoric water (10‰).

The rainfall samples with higher d-excess value are sampled at 8:00 am, while the rainfall samples with lower d-excess values are sampled at noon or in the afternoon during two plum rainfall events. This is mainly related to the occurrence time of precipitation. When the precipitation events occur in the evening, the main meteorological features in this period are low temperatures and low saturated vapor pressure. The relative humidity of air can easily reach the saturated vapor pressure indicating equilibrium fractionation occurring more easily, and the process of equilibrium fractionation does not change the values of d-excess. Therefore, the raindrops in the process of falling or on the ground are less affected by evaporation fractionation. Conversely, when the precipitation events occur in the daytime, the high temperatures and high saturated vapor pressure will make the relative humidity of air distant from the saturated vapor pressure. The non-equilibrium evaporation becomes the dominant factor influencing the decrease of the value of d-excess.

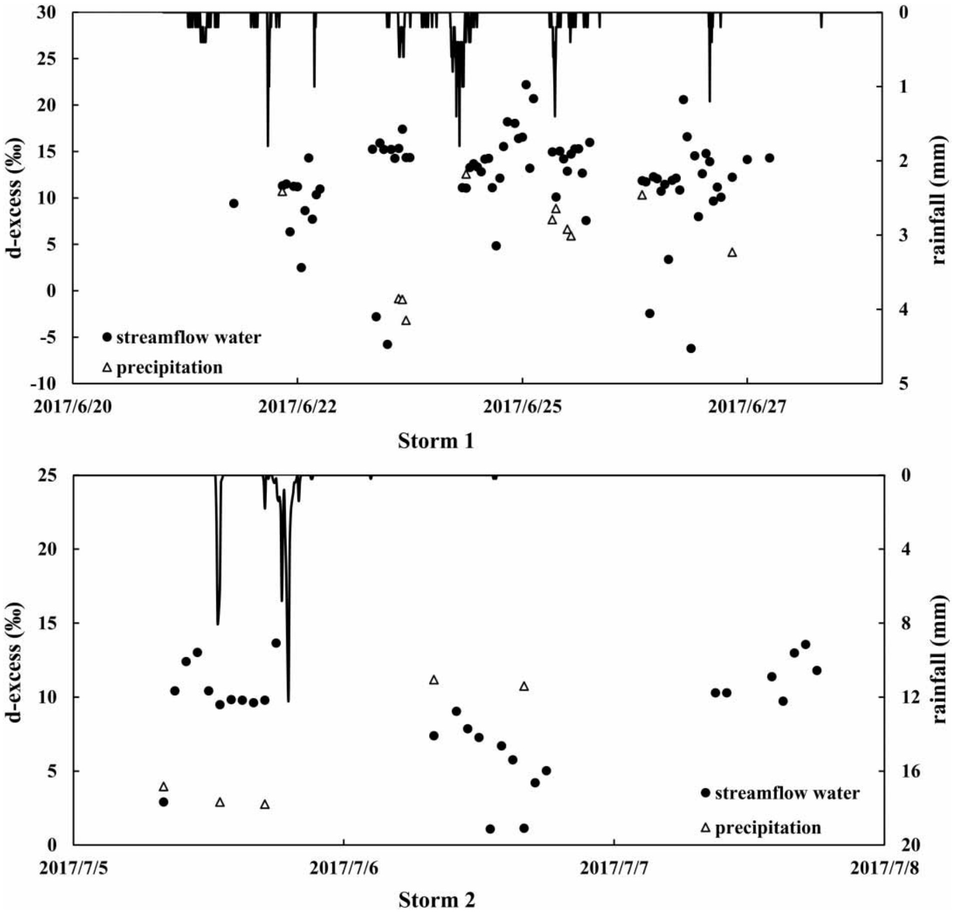

Fig. 5. Variation in d-excess values of precipitation and streamflow water during storm 1 and storm 2 in Hemuqiao watershed.

The temporal variation of d-excess of the streamflow water samples during the period of storm 1 and storm 2 are shown in Figure 5. The variation of d-excess of streamflow water is also significant and ranges from −5.78‰ to 17.40‰ for storm 1 and 1.08‰ to 13.14‰ for storm 2. The arithmetic mean value of d-excess is 10.55‰ for storm 1 and 8.91‰ for storm 2 which is close to the d-excess of the average global meteoric water (10‰) indicating slight evaporation fractionation. However, there are some points with low d-excess, which might be the influence of the evaporation fractionation. The raindrops falling on the watershed are enriched in heavy isotopes resulting from evaporation fractionation, and subsequent concentration to stream channel can also make the d-excess of the streamflow water change significantly.

There are significant differences in the d-excess values between the streamflow water and rainfall. The values of d-excess of the streamflow water are obviously distributed around the global meteoric water, however, the d-excess values of most rainfall samples are below 10‰. In this study, we use the isotopic composition of the streamflow water before the plum rainfall events to represent the isotopic composition of the pre-event water, and the value of d-excess of the pre-event is 11.50‰ for storm 1 and

11.64‰ for storm 2, respectively. The d-excess values of pre-event are slightly higher than those of streamflow water, but closer to the d-excess value of streamflow compared with that of rainfall during the plum rainfall events. This also provides convincing general evidence that the streamflow water in the headwater catchment is recharged not only mainly by precipitation but also by pre-event water during the plum rainfall events.

Mixing of various water sources and exchanging with surrounding rocks are the main factors affecting the d-excess values of pre-event water. The d-excess values of rainfall change with season, lower value in summer because of the intense evaporation fractionation, and in contrast, the d-excess value of rainfall in winter is high. The infiltrated precipitation gradually mixes well after entering the soil layer which makes the d-excess value of pre-event more stable. The soil water and groundwater stored in the watershed exchange oxygen isotopic composition with the surrounding rocks (Gat, 2003). The exchange effect makes the oxygen isotopic composition in the water more enriched, but the effect on the hydrogen isotopes can be negligible, which obviously increases the d-excess value of the pre-event water.

Conclusion

Based on measuring the stable isotopic composition of precipitation, soil water, and streamflow water samples in Hemuqiao watershed, which is covered with bamboo, we studied the influencing factors affecting the variation in isotopic composition of various water sources. The LMWL which was established by using the data of isotopic composition of precipitation is slightly different from the GMWL and meteoric water line of China. This is mainly related to the characteristics of the plum rainfall events, conditions of the water vapor source, and meteorological conditions in Hemuqiao watershed. The trend in isotopic composition of precipitation is mainly related to exchange between raindrops and environmental vapor, evaporation fractionation, and rainfall intensity. The isotopic variation of shallow soil water is more enriched than that of precipitation, indicating that canopy interception by bamboo, ground evaporation, and mixing with pre-event water play an important role in the variation of isotopic value of δ^{18}O. The variation range of the isotopic composition of deep soil water is relatively small indicating the slight influence of rainfall. The isotopic composition of streamflow water is the most enriched in comparison with other water resources, and the variation range is significantly low indicating it is recharged not only by these plum rainfall events. The d-excess differences between streamflow and rainfall indicate that streamflow water in Hemuqiao watershed is mainly recharged by pre-event water and precipitation during the plum rainfall events.

The results of the variation in stable isotopic composition of various water sources suggest some new research directions. First, the various rainfall intensity and heterogeneous distribution of rainfall on the upland headwater watershed can produce different results. Hence, studying the heterogeneous distribution (in temporal and spatial) of rainfall will improve our understanding of the runoff generation mechanism. Second, the d-excess differences between streamflow and rainfall indicate that streamflow water is mainly supplied by pre-event water and precipitation. How old is the pre-event water? It is another question waiting to be answered, which may also be a limitation of the article. More reasonable sampling methods for understanding the effect of the temporal variation of stable isotopic composition in precipitation in humid watershed are necessary.

Acknowledgments

The study is financially supported by the National Key Research and Development Program of China (2016YFC0402703), the National Natural Science Foundation of China (No. 41371048, 51479062), the Fundamental Research Funds for the Central Universities (2017B10914).

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Received 16 June 2018; accepted in revised form 3 December 2018. Available online 7 February 2019