

Isotopic analysis of water cycle elements in different land covers in a small headwater watershed

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Abstract

In this study, comparisons of isotopic variation of rainfall, throughfall, surface water, and groundwater were conducted in the Meilin watershed, which represents two different land uses, chestnut wood and bamboo. Also, isotopic differences between rainfall and throughfall were identified in these sub-watersheds. The results showed that the isotopic value of incremental rainfall, incremental throughfall and surface water exhibited a marked temporal variation in the selected sub-watersheds. The throughfall isotopic variation range was smaller than that of rainfall, which may result from the different production process between rainfall and throughfall. However, the isotopic composition difference between rainfall and throughfall resulting from different land uses was insignificant. The range of isotopic composition variation of surface water was not the same as that of rainfall, indicating that surface water came from a mix of precipitation and water stored before the rainfall event. The temporal variation of the isotopic composition of groundwater was small, implying that the influence of different land uses on groundwater isotopic composition was insignificant. The total variation range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of groundwater was smaller than that of surface water and sequential incremental rainfall, which means the $\delta^{18}\text{O}$ of groundwater can be replaced by that of base flow before the event in the hydrograph separation.

Keywords: Different land uses; Rainfall; Stable isotope; Temporal variation; Throughfall

Introduction

Industrial and agricultural development has increased at an unprecedented rate over the past 20 years, causing dramatic change of land use and land cover patterns in basins on a global scale. The influence of different land use/cover on hydrological processes is one of the most important science problems in

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hydrology research. The effect of land use and land cover change (LUCC) on Earth resources, environment, and sustainable development has received extensive attention (Potter, 1991; Vorosmarty *et al.*, 2000). On a basin scale, land use alters the land cover. LUCC will alter the balance of supply-and-demand of water resources and water quality through the influence on water cycle elements, i.e., evapotranspiration, interception, depression storage, infiltration, runoff generation, and concentration processes, which will, in turn, affect the ecosystem, environment, and economy. As a result, a better understanding of the hydrologic response of LUCC is of critical importance for water resources planning, management, and regional sustainable development.

Common techniques used for evaluating the effect of LUCC on hydrological response include the paired watershed approach (Schnorbus & Alila, 2004). With the development of computer technology, the basin hydrological model has been cited by many researchers as the most effective way to assess the influence of land use and land cover on hydrological response on the whole catchment scale since the 1970s (Yuan & Shi, 2001; DeFries & Eshleman, 2004; Zhang *et al.*, 2004; Burns *et al.*, 2005; Wang *et al.*, 2006). The lack of consideration of the pathways of runoff, basin residence time, and composition of runoff in the hydrological model creates a need to link internal hydrological processes with LUCC. The dynamic characteristics of free water storage volume can be obtained from the simulated hydrograph of the outlet section. The stable isotopes of water molecules, D (^2H) or ^{18}O , are affected by different water source mixing and physical processes such as evaporation and condensation, which compose isotope fractionation and result in the variation of isotope composition. Among those influencing factors, different water source mixing is the main element.

The stable isotope of water has been used to provide information about material transportation and the mix of precipitation and basin storage volume, which makes it pervade in many fields of hydrology study (Kendall & McDonnell, 1998; Wang, 2002). Most studies that use the stable isotope have focused on the analysis of the isotopic value change trend of precipitation, river water, and groundwater (Zhang & Yao, 1998; Longinelli & Selmo, 2003), the age and source of groundwater supply, groundwater resources evaluation (Kattan, 1997; Gu *et al.*, 2002), tracer of the flow path (Asano *et al.*, 2002; McGlynn *et al.*, 2002; Song *et al.*, 2002; Gu *et al.*, 2003; Hu *et al.*, 2007b), and the transformation of surface water and groundwater (James *et al.*, 2000; Gurrieri & Furniss, 2004; Zhang *et al.*, 2005; Bao *et al.*, 2007; Hu *et al.*, 2007a; Song *et al.*, 2007, 2009). Yet, little is known about the isotopic variation of water cycle elements in different land covers and how to use the stable isotope to evaluate the influence of land use/cover change on the process of runoff generation and concentration (McDonnell *et al.*, 1990, 1991; Ogunkoya & Jenkins, 1991; Pionke *et al.*, 1993; Kubota & Tsuboyama, 2003). The purpose of this study was to compare the isotope composition of rainfall, throughfall, surface water, and groundwater and identify the isotopic difference between throughfall and rainfall in different land covers. The further purpose is to better understand the rainfall-runoff mechanism under different land covers. To achieve this, two areas, chestnut and bamboo, of the Meilin watershed were selected for sample collection and isotopic analysis.

Study area and methods

Hydrological settings of the study area

This study was conducted in a first-order watershed, Meilin (0.737 km²), within the Taihu Lake drainage basin in the eastern part of Yixian, China (Figure 1). The watershed is located in a lower mountain

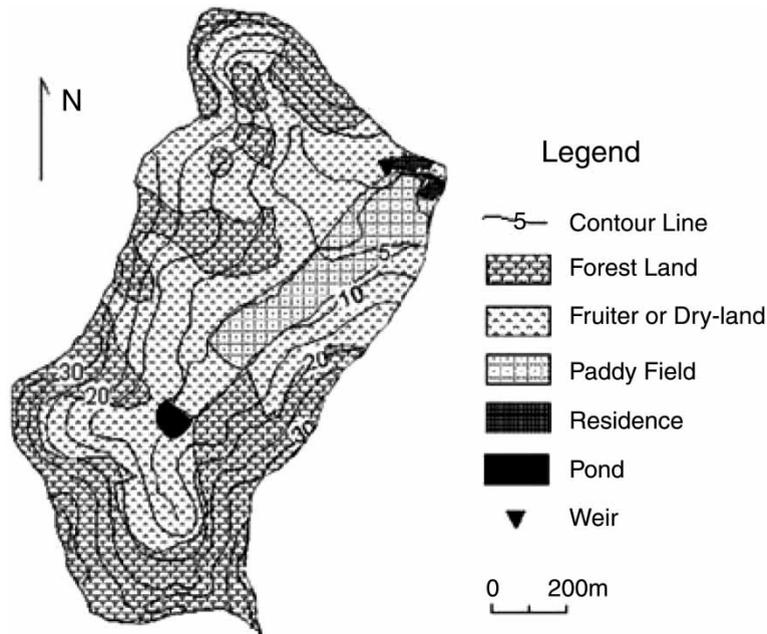


Fig. 1. Land use and topographic map of Meilin watershed.

area with a clear divide and the elevation varies from 2.7 to 45.9 m above the sea level. The annual average precipitation during the period from 1980 to 2000 was 1,177 mm. The mean annual air temperature is 15.7 °C and the subtropical monsoon climate makes it mild and humid. The dominant wind direction is southeast in the summer and northwest in the winter. Two tributaries converge to the outlet of the watershed without stream flow during most times of the year. The zonal soil types are red-yellow soil and paddy soil. Typical land use in Meilin watershed could be classified as wetland, dry-land, bamboo, chestnut wood, vegetation land, and tea garden.

Sampling and analysis methods

A typhoon event that occurred on August 8, 2012 was selected for the Meilin watershed analysis. Rainfall, throughfall, surface water, groundwater, river discharge, and meteorological data were monitored and sampled in the chestnut and bamboo areas. In addition, their isotopic values were analyzed for comparison of the difference caused by different land uses.

Precipitation was monitored using a tipping bucket rain gauge installed in the watershed. Bulk rain-water was collected in the chestnut area with a 50-cm-diameter stainless barrel. In addition, modified versions of Kennedy *et al.*'s (Kennedy *et al.*, 1979) sequential rainfall sampler (Figure 2) were used for sampling incremental rainfall and throughfall in the storm event. The stainless barrel and sequential sampler for rainfall were placed in the same location in open spaces without plants on top of them. The sequential throughfall sampler was set under a chestnut tree or bamboo (Figure 1). The water was collected by using a 22-cm-diameter plastic funnel flowing into the bottle from the upper tube and flowing out of the lower tube till the bottle was filled up. The bottle size for rainfall and throughfall was 280 ml,

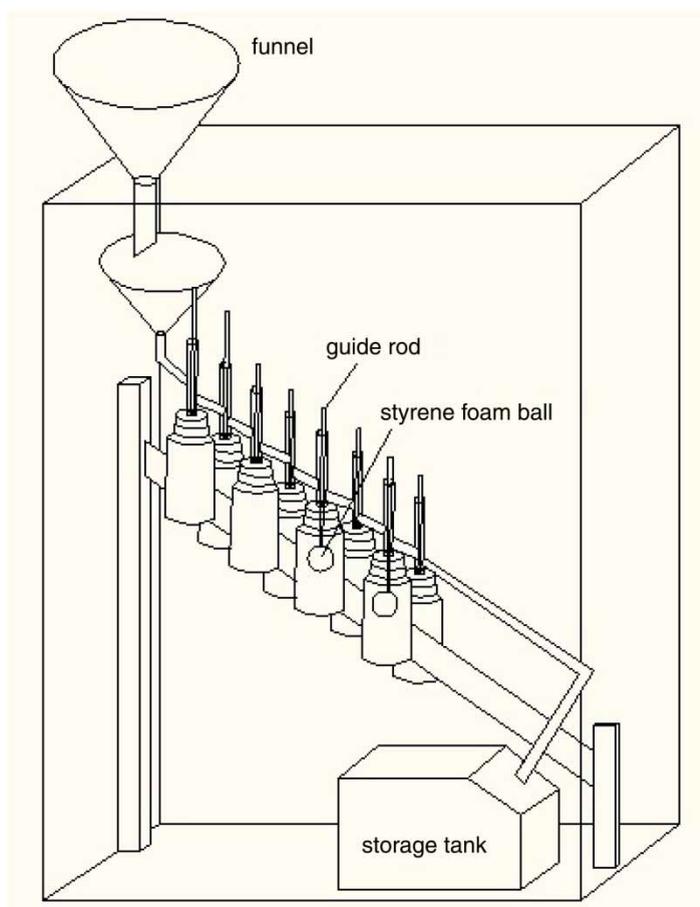


Fig. 2. Schematic diagram of sequential rainfall and throughfall sampler.

representing 1.84 mm of sampling water, which was calculated by dividing the bottle volume by the sectional area of the funnel. Each sampler consisted of eight bottles. It should be noted that precipitation in the bamboo area was calculated by the total volume of the barrel, since an air pipe of the sequential rainfall sampler was broken due to strong rainfall intensity, which resulted in the missing of several samples and inaccuracy of the rainfall volume.

Surface water samples were collected hourly using a 1-m³-bulk sink located at the outlet of the chestnut area. Groundwater was sampled hourly by a monitoring well installed beside the sink (3.0–5.0 m below the surface) during the event.

Streamflow was monitored continuously and sampled hourly at 90° thin-plate gauging weirs at the outlet of the Meilin watershed. Surface water, groundwater and streamwater during runoff were sampled once before the event, hourly during the storm, and once after the event.

The collected samples were analyzed for isotopic compositions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ using mass spectrometry (MAT 253). Water samples were prepared for $\delta^{18}\text{O}$ analysis by using the $\text{CO}_2\text{-H}_2\text{O}$ equilibrium method, and for deuterium analysis by using the $\text{H}_2\text{-H}_2\text{O}$ equilibrium method with a platinum catalyst added. The isotopic compositions were reported in δ -notation as parts per mil (‰) relative

to Vienna Standard Mean Ocean Water. The accuracies of measurements are $\pm 0.2\text{‰}$ for oxygen-18 and $\pm 2\text{‰}$ for deuterium.

Results and discussion

The isotopic values of precipitation and throughfall ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) are shown in Tables 1 and 2.

Isotopes of precipitation

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of sequential incremental rainfall in the chestnut and bamboo areas in Meilin Basin during typhoon event 20120808 are presented in Figure 3 and Table 1. Isotopic values of incremental precipitation exhibited marked temporal variation in the two experimental areas. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation during the storm in the chestnut area ranged from -84‰ to -43‰ and -11.4‰ to -6.5‰ , respectively. The average of volume-weighted and arithmetic mean values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of incremental precipitation were -59‰ and -8.4‰ . Because of the small number of collected samples and the same volume of every bottle, the values of volume-weighted and arithmetic mean were almost the same. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values during the storm in the bamboo area ranged from -90‰ to -53‰ and -12.7‰ to -7.3‰ , respectively. The average of volume-weighted and arithmetic mean values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of incremental precipitation were -73‰ and -10‰ , -74.5‰ and -10.2‰ , respectively. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values during the storm exhibited great changes.

Many studies showed that short-term isotopic fluctuation in precipitation was affected by rainfall intensity, moisture sources, cloud structure, and wind velocity, etc. (Pionke & DeWalle, 1992).

Precipitation enriched in light isotope due to large amounts of rainfall and values of relative humidity as well as little evaporation, is usually recognized as the ‘amount effect’ of precipitation. That means

Table 1. The statistics of isotopic values of precipitation in different land covers.

Types of land use	Rain (mm)	$\delta\text{D}(\text{‰})$				$\delta^{18}\text{O}(\text{‰})$			
		Min	Max	Ave	Range	Min	Max	Ave	Range
Chestnut	21.3	-84.7	-43.8	-59.7	40.9	-11.4	-6.5	-8.4	4.9
Bamboo	50.5	-90.5	-53.1	-74.5	37.4	-12.7	-7.3	-10.2	5.4

Range: The value of column range equals maximum value minus minimum value.

Table 2. The statistics of isotopic values of throughfall in different land covers.

Types of land use	Rain (mm)	$\delta\text{D}(\text{‰})$				$\delta^{18}\text{O}(\text{‰})$			
		Min	Max	Ave	Range	Min	Max	Ave	Range
Chestnut	14.2	-51.2	-50.5	-50.9	0.7	-7.2	-7.2	-7.2	0.0
Bamboo	44.2	-84.2	-57.0	-65.4	27.2	-11.5	-7.1	-8.8	4.4

Range: The value of column range equals maximum value minus minimum value.

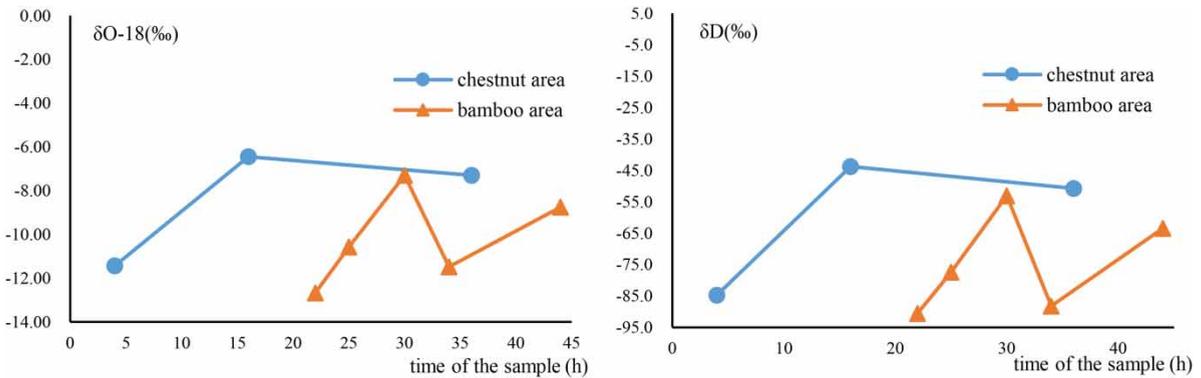


Fig. 3. Isotopic variation of precipitation in different land covers.

rainfall with higher intensity has more negative isotopic values than that with lower intensity. The spatial distribution of rainfall was highly heterogeneous due to the strong local property of the typhoon event. Precipitation in the bamboo area was more than twice as much as precipitation in the chestnut area during the same event. The large difference in the rain capacity in these two areas explained the difference in their isotopic values.

Isotopes of throughfall

The isotopic value of $\delta^{18}O$ and δ^2H for incremental throughfall in the chestnut and bamboo areas in the Meilin Basin during typhoon event 20120808 are presented in Figure 4 and Table 2. The arithmetic mean values of throughfall in both the chestnut area and bamboo area were larger than those of direct rainfall (Tables 1 and 2). For the example of $\delta^{18}O$, in the chestnut area, the arithmetic mean value of throughfall was -7.16‰ , which was larger than that of direct rainfall. The same situation occurred in the bamboo area (-8.81‰ for throughfall and -10.16‰ for direct rainfall). This is caused by the fact that more heavy isotope accumulates in throughfall compared to rainfall, as throughfall involves the process of interception of the forest canopy resulting in longer lag time and evaporation time.

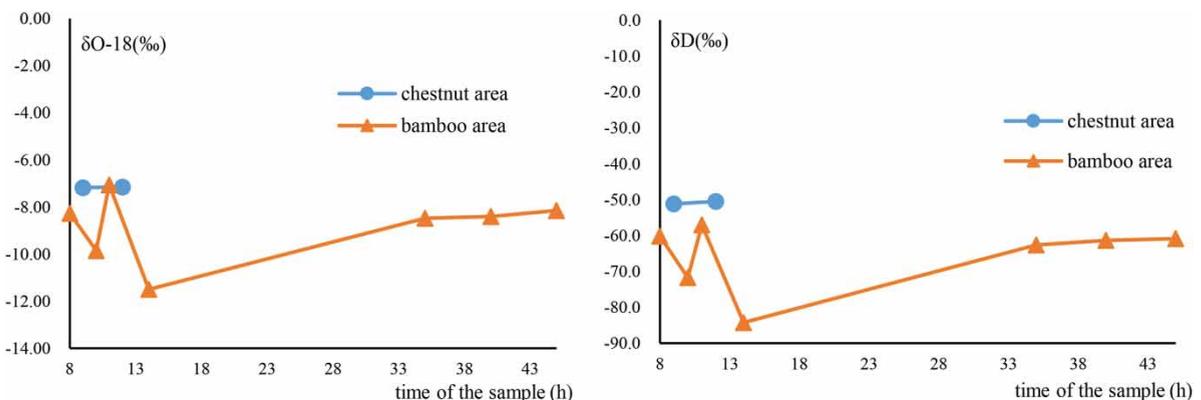


Fig. 4. Isotopic variation of throughfall in different land covers.

Isotopic values of incremental throughfall showed less temporal variation than that of incremental rainfall (Tables 1 and 2). For example, in the bamboo area, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of incremental direct rainfall were 37.42‰ and 5.37‰, and those of incremental throughfall were 27.21‰ and 4.44‰. This may result from the interception of the forest canopy for throughfall, which can cause a retention effect. It means that, compared with rainfall, throughfall has a longer lag time and evaporation time, that will result in a different isotopic value of throughfall.

Isotopic difference between rainfall and throughfall

The isotopic differences resulting from calculation methods and sampling methods for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of rainfall and throughfall in different land uses are calculated in Table 3. Results show that the isotopic value of throughfall was more positive than that of rainfall during the 20120808 storm event. This is mainly due to the fractionation processes in the catchment. That is to say, in the forest area, part of the precipitation is stored in the canopy. This water is subjected to evaporation and the isotopic exchange with the water vapor in the air. This physical fractionation depends on the air temperature, relative humidity and the ^{18}O difference between the rainfall and the water vapor in the air.

Throughfall is produced after the rainfall reaches the forest canopy and drips with the canopy interception, which leads to interception losses. The interception losses of different vegetation vary due to the different leaf areas. This causes the different variation between rainfall and throughfall in different land uses. In this study, the isotopic difference between rainfall and throughfall resulting from different land covers was small. Taking the volume-weighted mean value of $\delta^{18}\text{O}$ as an example, the isotopic difference between throughfall and rainfall in the chestnut area was 1.2‰, which was larger than that of the bamboo area (1.1‰). This is due to the fact that the areas of different land uses were influenced by a combination of meteorological factors and leaf areas, which led to the smaller amount of rainfall and larger interception loss in the chestnut area than those of the bamboo area.

Isotopes of surface water

The isotopic differences in surface water during the 20120808 storm event in the Meilin watershed are presented in Table 4 and Figure 5. The isotope values of surface water in different land uses all showed remarkable temporal variation. Taking $\delta^{18}\text{O}$ as an example, the value in the chestnut area ranged from -12.1‰ to -6.8‰ , which was greater than that of the bamboo area (-10.7‰ to -7.5‰).

The fact that the variation range of surface water was different from that of rainfall indicated that surface water results from the mixing of precipitation and water stored before the event rather than

Table 3. The statistical variation of isotopic values between precipitation and throughfall in different land covers.

Event No.	Types of land use	Rain (mm)	$\delta\text{D}(\text{‰})$			$\delta^{18}\text{O}(\text{‰})$		
			ATF-AP	VTF-VP	VTF-OP	ATF-AP	VTF-VP	VTF-OP
20120808	Chestnut	21.3	8.9	8.9	10.1	1.2	1.2	0.9
	Bamboo	50.5	9.1	7.4	1.3	1.4	1.1	0.6

TF means sequential throughfall, OP means bulk precipitation, P means sequential precipitation, prefix 'A' means arithmetical averaging, 'V' means volume-weighted.

Table 4. The statistics of isotopic values of surface water in different land covers.

Types of land use	Rain (mm)	$\delta D(\text{‰})$				$\delta^{18}\text{O}(\text{‰})$			
		Min	Max	Ave	Range	Min	Max	Ave	Range
Chestnut	21.3	−89.1	−48.1	−71.0	41.0	−12.1	−6.8	−9.7	5.3
Bamboo	50.5	−78.7	−51.7	−64.5	27.0	−10.7	−7.5	−9.19	3.2

Range: The value of column range equals maximum value minus minimum value.

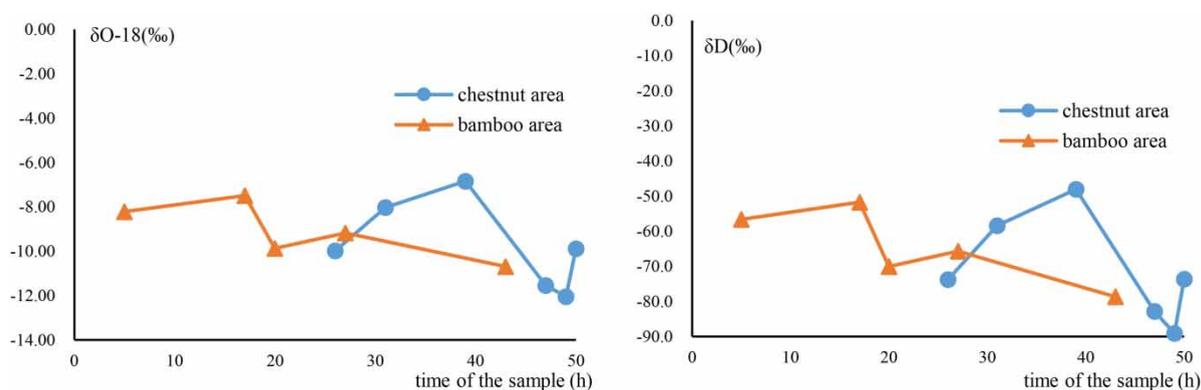


Fig. 5. Isotopic variation of surface water in different land covers.

precipitation alone. In the chestnut area, the value of $\delta^{18}\text{O}$ of rainfall ranged from -11.4‰ to -6.5‰ with a variation range of 5.0‰ and the arithmetic mean value was -8.4‰ . The value of $\delta^{18}\text{O}$ of surface water ranged from -12.1‰ to -6.8‰ with a variation range of 5.2‰ and the average of the arithmetic mean value was -9.7‰ . The $\delta^{18}\text{O}$ average of surface water was more negative than that of rainfall, which means there were other sources of surface water, for example, the water stored before the event, which had a $\delta^{18}\text{O}$ value of -11.6‰ .

In the bamboo area, the value of $\delta^{18}\text{O}$ of rainfall ranged from -12.7‰ to -7.3‰ with a variation range of 5.4‰ and the arithmetic mean value was -10.2‰ . The value of $\delta^{18}\text{O}$ of surface water ranged from -10.7‰ to -7.5‰ with a variation range of 3.2‰ and the arithmetic mean value was -9.1‰ . The average of the latter was more positive than that of the former because the value of $\delta^{18}\text{O}$ of surface water before the event was -9.9‰ , which was more positive than that of precipitation.

In addition, the arithmetic mean value for precipitation (-8.4‰) in the chestnut area was more positive than that in the bamboo area (-10.2‰). However, the arithmetic mean value of surface water exhibited a contrary tendency (chestnut -9.7‰ , bamboo -9.1‰). On the other hand, the $\delta^{18}\text{O}$ value of water before the event in the chestnut area was -11.6‰ , more negative than that in the bamboo area. The result fully indicated that surface water partly comes from water stored before the event.

Isotopes of groundwater

The isotopic change of groundwater during the 20120808 storm event in the Meilin watershed is presented in Table 5 and Figure 6. The change of $\delta^{18}\text{O}$ in groundwater may have resulted from preferential

Table 5. The statistics of isotopic values of groundwater in different land covers.

Types of land use	Rain (mm)	$\delta D(\text{‰})$				$\delta^{18}\text{O}(\text{‰})$			
		Min	Max	Ave	Range	Min	Max	Ave	Range
Chestnut	21.3	-46.2	-41.8	-44.5	4.4	-7.4	-5.7	7.0	1.7
Bamboo	50.5	-45.8	-43.9	-44.4	1.9	-7.3	-6.7	-7.1	0.6

Range: The value of column range equals maximum value minus minimum value.

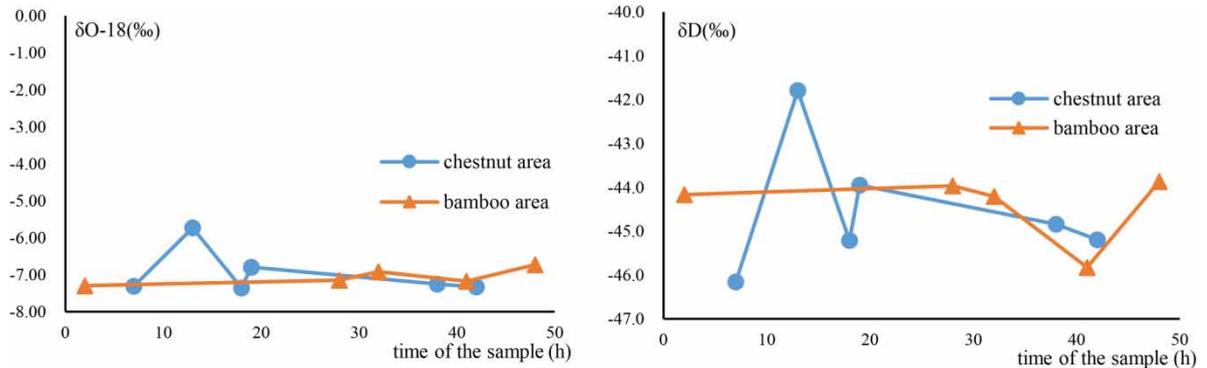


Fig. 6. Isotopic variation of groundwater in different land covers.

isotopically heavier water, soil water and rainfall, which made the temporal variation of isotopic composition of groundwater small. In the chestnut area, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater ranged from -46‰ to -41‰ and -7.4‰ to -5.7‰ with the arithmetic mean values of -44‰ and -7.0‰ , respectively. In the bamboo area, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater ranged from -46‰ to -44‰ and -7.3‰ to -6.7‰ with the arithmetic mean values of -45‰ and -7.1‰ , respectively. The small difference between the arithmetic mean isotopic values of groundwater in the two experimental areas indicated that the influence of different land uses on the groundwater isotopic value is not significant.

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values spanned a total range of 4‰ and 1.6‰ in the chestnut area, which were greater than those ranges in the bamboo area ($\delta^2\text{H}$: 2‰ ; $\delta^{18}\text{O}$: 0.5‰). However, the variation range of surface water (chestnut area: $\delta^2\text{H}$ 41‰ and $\delta^{18}\text{O}$ 5.2‰ , bamboo area: $\delta^2\text{H}$ 27‰ and $\delta^{18}\text{O}$ 3.2‰) and sequential rainfall (chestnut area: $\delta^2\text{H}$ 41‰ and $\delta^{18}\text{O}$ 5.0‰ , bamboo area: $\delta^2\text{H}$ 37‰ and $\delta^{18}\text{O}$ 5.4‰) were larger than that of groundwater, which is shown in Figures 7 and 8. The small temporal variation of groundwater isotopic composition supported the conventional assumption to use the pre-event baseflow $\delta^{18}\text{O}$ as the groundwater $\delta^{18}\text{O}$ in the Meilin watershed for the hydrograph separation. Because the hydrograph is divided into surface water and groundwater with the two-source hydrograph separation, and in this study, the total variation range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ was smaller than that of surface water, which led to the small variation range of groundwater, it is reasonable to use the isotope of the pre-event base flow to replace that of groundwater.

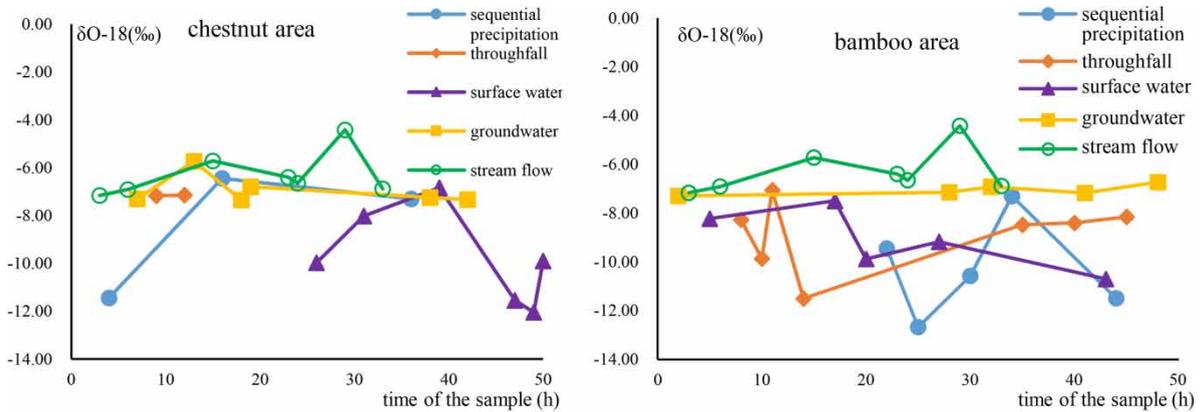


Fig. 7. Isotopic variation of water cycle elements in different land covers (O-18).

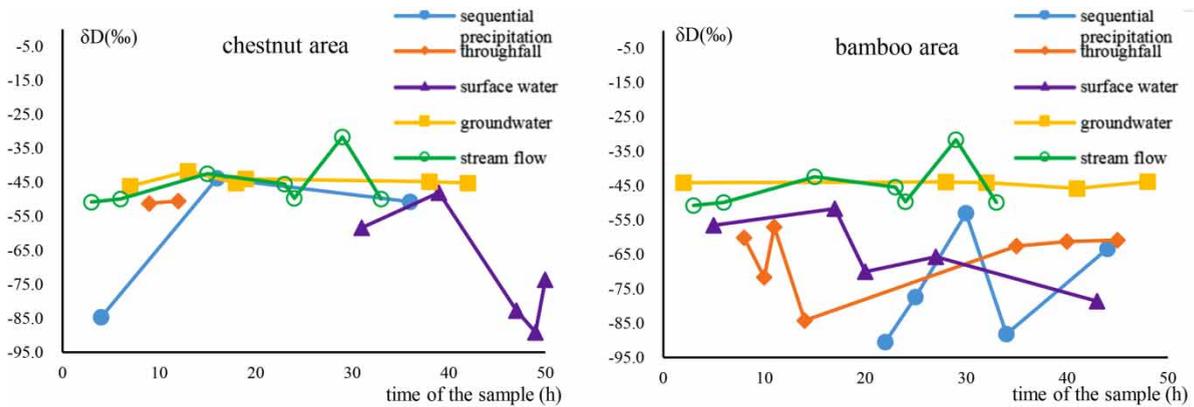


Fig. 8. Isotopic variation of water cycle elements in different land covers (D).

Conclusions

This study was conducted in the Meilin watershed for a typhoon event, 20120808. Isotopic analysis and variations in different land uses were investigated by sampling total rainfall, sequential rainfall, sequential throughfall, surface water, groundwater, and streamflow in two experimental areas.

The isotopic values of incremental rainfall exhibited significant temporal variation. Larger rainfall led to the lighter isotope value, which corresponded to the ‘amount effect’ of precipitation. The isotopic value of throughfall was more positive than that of rainfall due to the interception of the forest canopy. The isotopic difference between rainfall and throughfall caused by different land covers was small. Taking the volume-weighted value of $\delta^{18}\text{O}$ as an example, the difference between throughfall and rainfall was 1.2‰ in the chestnut area and in the bamboo area the difference was 1.1‰.

The isotopic values of surface water exhibited marked temporal variation. However, the variation range was not the same as that of rainfall, which revealed that surface water originated from the mixing of pre-event water and rainfall. The small isotopic temporal variation of groundwater showed

that different land uses have a small effect on the isotope of groundwater. For example, the variation range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of groundwater was 4‰ and 1.6‰ in the chestnut area and 2‰ and 0.6‰ in the bamboo area. The results obtained in this study need further verification with more storms in different seasonal floods, different land covers and different flood types.

The results provide basic data and a new research method for an accurate and quantitative investigation of the hydrological process of LUCC, which, furthermore, has important theoretical significance and guiding value in understanding the mechanism of runoff generation and concentration, parameter calibration of the hydrological model, and the advancement of accuracy and early warning of flood forecasting.

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