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# Characteristics of $\delta^{18}$O and $\delta^{2}$H and their implication for the interaction between precipitation, groundwater and river water in the upper River Tuojiang, Southwest China

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## Abstract

The Tuojiang River has multiple water sources and serious pollution problems, but its hydrological mechanism in the upper reaches is still unclear. To better understand the hydrological characteristics of the Tuojiang River, the isotopic compositions of its precipitation, river water and groundwater in the upper reaches have been investigated from May 2018 to April 2019. The results indicated that the isotope values of precipitation, river water and groundwater fluctuate significantly throughout the year with depleted value in the wet season and enriched value in the dry season. Spatially, the isotope values of river water increase gradually from upstream to downstream. River water is the main source of recharge to groundwater and precipitation is the minor one. The isotope-based hydrograph separation shows that the Mianyuan River and Pihe River contribute more greatly to Tuojiang River than the Shiting River and Yazi River. The mean residence time of river water from the Tuojiang River varies from 0.95 to 1.49 years, which indicates that rivers in the upper reaches of the Tuojiang River respond to precipitation quickly. This study proved the usefulness of stable isotopes to identify the different water cycle components and reflect the pollution problem in multiple water source confluence areas.

**Key words:** environmental protection, hydrograph separation, hydrology, *MRT*, stable isotope, Tuojiang River Basin

## Highlights

- Analysis of the spatio-temporal characteristics of isotope values in the Tuojiang River Basin.
- Exploration of the seasonal variation of recharge source to groundwater in the Tuojiang River.
- Analysis of the temporal variation in the relative contribution of tributaries over total river flow.
- Estimation of the mean residence time of the Tuojiang River and its tributaries.

## INTRODUCTION

'Isotope' refers to an element with the same number of protons and different numbers of neutrons; they can be divided into radioisotopes and stable isotopes. With the development of measurement technology, the stable isotope has been widely applied and developed in different fields and plays an important role, especially in the study of food, chemistry, biology and hydrology, etc. (Meitinger *et al.* 2014; Stout *et al.* 2014; Zhao *et al.* 2014; Xia *et al.* 2019a). The research and application of the stable isotope in hydrology began in the 1950s. Craig (1961) proposed the global meteoric water line ($\delta^{2}H = 8\delta^{18}O - 10$) by analysing the oxygen and hydrogen isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$) in different waters all around the world; then, Dansgaard (1964) gave a definition to the deuterium excess (*d-excess* $= \delta^2H - 8\delta 18O$); Gat (1996) found that when the ocean or other water bodies evaporate, they will undergo isotope fractionation, and the light isotopes in the water will escape first, thus increasing the specific heavy isotopic content, resulting in the constant accumulation of heavy isotopes.

Due to the fractionation, natural stable isotopes in different waters have different composition characteristics and evolution laws and vary greatly at the spatial-temporal level. The natural stable isotope is viewed as the fingerprint of water, thus in some remote areas where hydrological data are insufficient, the isotope data can be studied as a way of supplementation. For example, Crawford *et al.* (2017) studied the isotopic composition of the precipitation of Macquarie Marsh in New SouthWales, Australia, and found that a large portion of the local precipitation comes from inland. Biggs *et al.* (2015) compared the isotopic compositions of four lakes in the arid region of the western Himalayas and found that lakes with a deeper depth have a greater evaporation ratio. With the development of modern industry and the increase in population, there is a growing demand for water resources. In some arid areas, water resources have already become a limiting factor for social development. So, the assessment of water quantity and quality appears important. The introduction of stable water isotopes as a tool for investigating storm hydrographs in a watershed started in the late 1960s (Crouzet *et al.* 1970). In the past 30 years, changes in oxygen and hydrogen isotopic compositions ($\delta^{18}O$ and $\delta^2H$) in watershed water have been proved to be able to identify the water source and hydrological paths under different flow conditions (Ogrinc *et al.* 2008, 2018; Zhao *et al.* 2011). Subsequently, the method was widely applied in various regions by many researchers; for example, Vasil'chuk *et al.* (2017) studied the contribution of snow meltwater, precipitation and groundwater to the runoff in different seasons of the Dzhankuat R. glacier. It was found that a considerable portion of Dzhankuat R. total runoff in June originated from spring snowfall, while in August and September, the contribution of runoff is mainly from groundwater, snow and glacial meltwater. Liu *et al.* (2008) performed hydrograph separation analysis on the Heishui River and its tributaries in the upper reaches of the Yangtze River by stable isotopes. The result shows that the base flow in the Heishui River Basin is mainly derived from snow and glacial melt water. Zhao & Li (2017) found by analyzing stable isotopes that with the increasing distance from the Yellow River, the supply from the Yellow River decreases and the supply from groundwater increases in the rivers in the Dezhou region. The interaction between precipitation, surface water, and groundwater plays an important role in the elaboration of water cycle mechanisms, which are of great significance in scientifically developing and managing water resources. However, it is difficult to investigate this cycle process by traditional methods (Hao *et al.* 2019). The stable oxygen and hydrogen isotopes are ideal conservative tracers to provide insight for investigating this cycle process as they are components of water molecules and remain unchanged except in instances of water phase changes or isotope fractionation in the hydrological cycle. In recent years, the pollution problems of lakes and rivers such as the Tuojiang River and Lake Taihu have become more and more serious (Chen *et al.* 2020a). Estimating the mean residence time and evaporation of lakes and rivers by analyzing stable isotope values can provide some insightful suggestions to understand the pollution situation and the renewal rate of water. By studying the stable isotope values of water in more than 1,000 lakes in the United States, Brooks *et al.* (2014) found that the lake water chemistry has a strong correlation with evaporation and a poor correlation with residence time, and the evaporation capacity of lakes with a good biological state is weaker than lakes with a poor biological state.

Located in southwest China, the Sichuan Basin has varied and complicated topography, a low-lying West and a high East. It is the source area of many important tributaries of the Yangtze River. Affected by multiple monsoons, complex water vapor source, and unique geographical and climatic characteristics, a complicated water circulation mechanism is observed in this region. Previous studies on the stable isotope in Sichuan Basin mainly were on the hydrological mechanism of mountain rivers and changes in rainfall isotope under the influence of monsoon (Xia *et al.* 2019b, 2019c). Isotopic study of the rivers in the Chengdu Plain is still rare. Furthermore, previous studies on the evaporation and replenishment of natural water bodies in the Plain are quite limited in both the sampling frequency and the duration of time. The mutual replenishment mechanism between different water bodies has been analyzed in many past studies (Yeh *et al.* 2010; Banks *et al.* 2011; Martinez 2015). However, few studies focused on tributary replenishment to the mainstream. The Tuojiang River is a typical river affected by human activities with complex water sources and seriously polluted water, flowing through densely populated and industrial areas. From May 2018 to April 2019, the authors conducted a one-year continuous sampling and measurement of isotopes in river water and groundwater along the upper reaches of the Tuojiang River. It provided high-precision isotope data for river water and groundwater as well as an important supplement to the isotope data set of the Tuojiang River Basin. The main purposes of this paper are: (1) to understand the variations of stable isotopes in rivers, precipitation, and groundwater in the upper reaches of the Tuojiang River Basin; (2) to identify the interaction between the river, groundwater, and precipitation in the upper reaches of the Tuojiang River Basin; (3) to obtain the contribution ratios of tributaries' recharge to the mainstream of the Tuojiang River; (4) to calculate and compare the *MRT* (mean residence time) of the mainstream of the Tuojiang River and its tributaries. The results of this paper will prove the usefulness of stable isotopes for separating components of the hydrological system and indicating the potential pollution situation in medium catchments with complicated sources and serious pollution problems.

## STUDY AREA

Tuojiang River is an upstream tributary of the Yangtze River (104 °E ~ 105.5 °E, 29 °N ~ 31.5 °N) (Figure 1). The Tuojiang River has five different tributaries in its upper reach. The upper tributaries include the Yazi River, Shiting River and Mianyuan River. These three tributaries flow southward and merge into the mainstream of Tuojiang River in Jintang County. The middle tributaries include the Pihe River and Qingbai River. The Qingbai River drains into the Pihe River before entering into Tuojiang River. The Qingbai River and Pihe River are derived from the Minjiang River system; thus, the water source of the Tuojiang River is complicated. The Tuojiang River has a total length of 712 kilometers and a drainage area of 32,900 square kilometers. The study region of this paper mainly includes the upper part of the Tuojiang River. The Tuojiang River Basin is located in a humid monsoon region with annual mean precipitation about 1,200 mm. Annual precipitation amount in the middle part of the river tends to be low (800 mm) and annual precipitation amount in the northwest mountains is much higher (1,300 mm). The Tuojiang River has a distinct dry and wet season, and the precipitation in the wet season accounts for more than 80% of the annual total (Figure 2).

## METHODS

### Sampling and isotope analysis

Water samples in the study area were collected from May 2018 to April 2019. During the wet season (May-October), the sampling was performed at a weekly frequency, and in the dry season (November-April), the sampling was performed at a bi-weekly frequency. A total of 30 sampling activities were conducted, with 714 samples overall, including 117 groundwater samples, 597 river water samples and 102 precipitation samples. A total of 20 sampling sections were laid in the study area, of which 16 were river water sampling sections and four were groundwater sampling sections. The sampling locations and names are shown in Table 1.

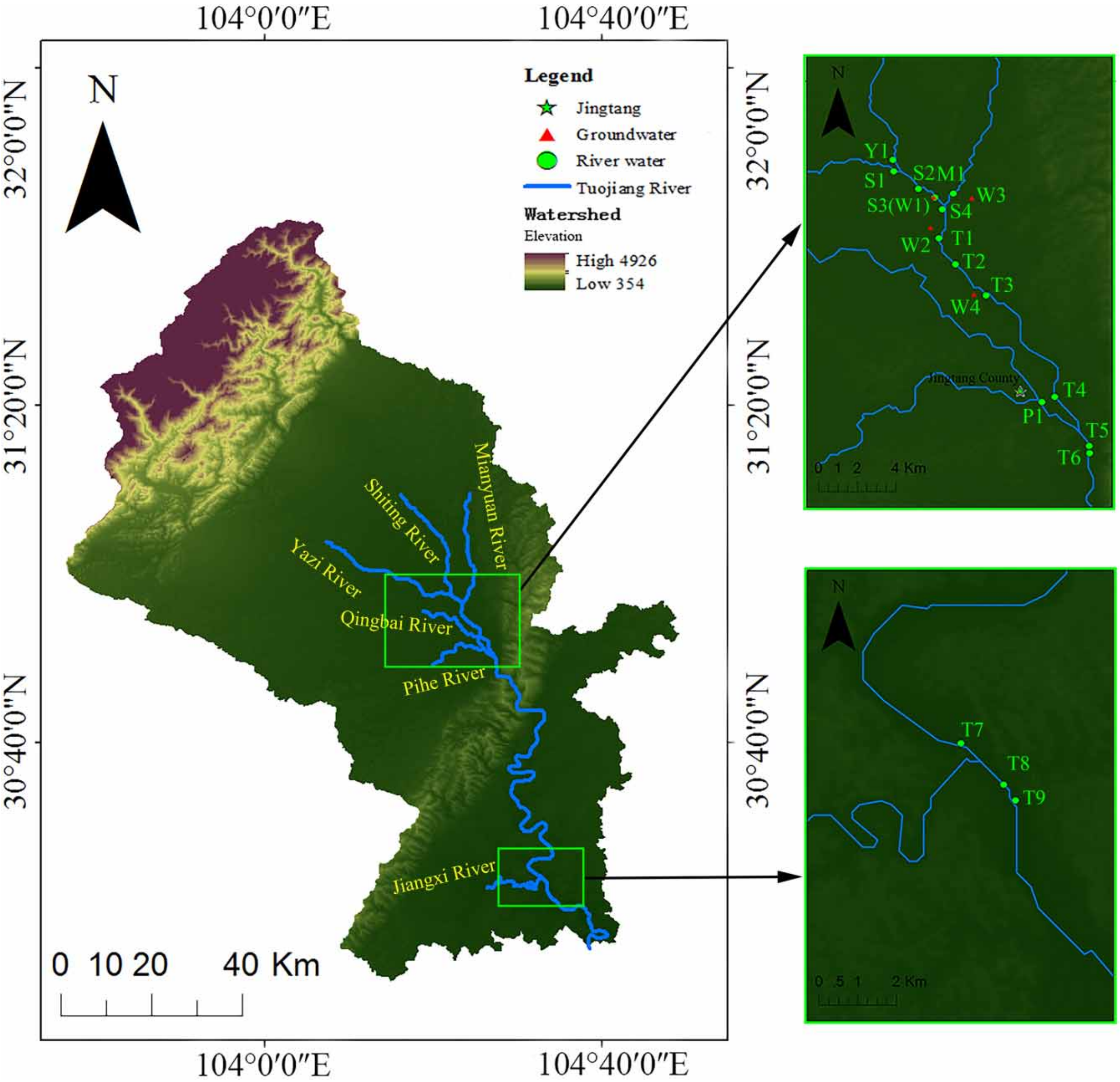

**Figure 1** | The location of the study region. Sampling sites of river water (circles), and groundwater (triangles) samples are shown. The Qingbai River merges into the Pihe River at P5.

The water samples collected from the upper reaches of the Tuojiang River include surface water, groundwater, and precipitation. The surface water samples were collected from the mainstream of the Tuojiang River and its four tributaries. The river water was collected in a one-liter plastic bottle, which was connected to a rope, and the river water 20 cm below the surface was selected via measuring the length of rope. Groundwater samples were pumped from residential wells along the Tuojiang River, which comes from a Quaternary phreatic aquifer with a depth of 5–20 metres. Because of the logistical limitations, it was difficult to collect the high-frequency precipitation in the study area. Therefore, the precipitation data collected from the State Key Laboratory of Hydraulics and Mountain River Engineering of Sichuan University were employed instead. The shortest distance between the precipitation sampling point (104.08 °E, 30.63 °N) and the Tuojiang River is 38 kilometers. The precipitation sampling device was made with reference to the recommended method of the Global Precipitation Isotope Network (GNIP) (http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html).

Water samples were stored in a 20 ml high-density polyethylene bottle with a tight screw cap. The sampling bottle was moistened and washed three times on site, and sealed with sealing film. Then, the water samples were stored quickly in the refrigerator. Because of unfavourable weather conditions and human factors, the number of samples per month may vary slightly. All water samples were

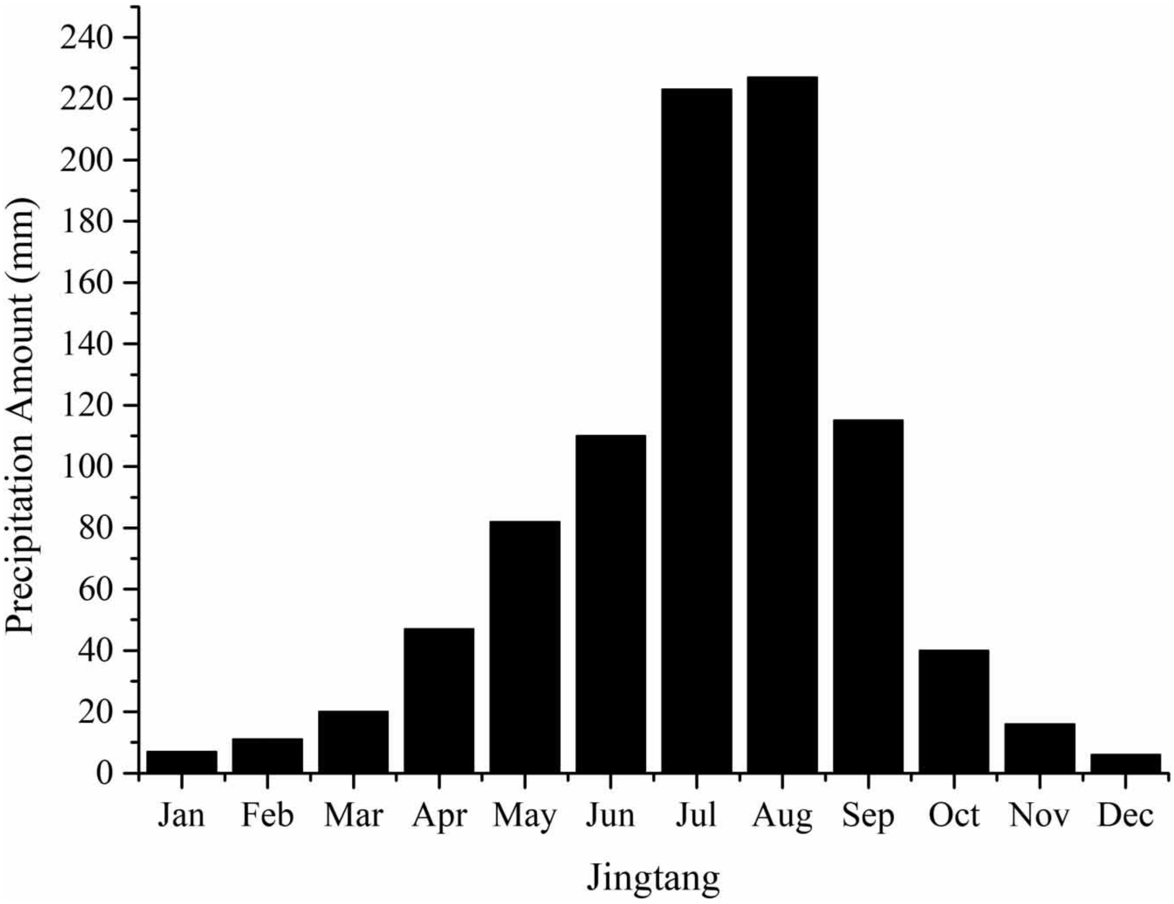

**Figure 2** | Average monthly precipitation for Jingtang county during 1981–2010.

**Table 1** | Sampling locations along the Tuojiang River and its tributaries

| Sample site | Type of water | Latitude (°) | Longitude (°) | Sample site | Type of water | Latitude (°) | Longitude (°) |
|---|---|---|---|---|---|---|---|
| S1 | River | 30.963447 | 104.3665806 | P1 | River | 30.85013611 | 104.4364889 |
| Y1 | River | 30.958 | 104.367 | T5 | River | 30.83016389 | 104.4597 |
| S2 | River | 30.94996667 | 104.37865 | T6 | River | 30.82621389 | 104.459625 |
| S3 | River | 30.945875 | 104.3863139 | T7 | River | 30.40393889 | 104.54495 |
| S4 | River | 30.94035278 | 104.3898694 | T8 | River | 30.39563333 | 104.5570194 |
| M1 | River | 30.94779722 | 104.3950111 | T9 | River | 30.39054167 | 104.55775 |
| T1 | River | 30.92748056 | 104.385575 | W1 | Groundwater | 30.94598889 | 104.3858694 |
| T2 | River | 30.91471944 | 104.3960694 | W2 | Groundwater | 30.93174444 | 104.384225 |
| T3 | River | 30.89633333 | 104.4073611 | W3 | Groundwater | 30.945575 | 104.4034611 |
| T4 | River | 30.85271111 | 104.4425 | W4 | Groundwater | 30.90050278 | 104.4046389 |

analyzed at the Institute of Water Resources and Hydropower, Sichuan University, by a triple-liquid water isotope analyzer which is manufactured by Los Gatos Research (LGR). The LGR analyzer uses spectrometry to measure the stable isotope content in water and its measurement principle is the OFF-AXIS Integrated Cavity Output Spectrometer (OA-ICOS). With the aid of a fully automatic sampler, the analyzer automatically and continuously measures the sample according to a computer program and filters the sample impurities by using a 0.45 $\mu$m filter before measurement. Each sample was measured six times and the first two measurements were discarded due to their large error, and only the average of the last four measurements was used. Reference standard samples based on VSMOW-2(Vienna Standard Mean Ocean Water) and SLAP-2 (Standard Light Antarctic Precipitation) were measured at intervals of three water samples to diagnose whether an abnormality occurred during the measurement. The isotopic composition of the water samples is expressed by the thousandth deviation from the Vienna standard average seawater, which is defined as follows:

$$\delta(‰) = (R_{sample} - R_{standard})/(R_{standard}) \times 1000 \tag{1}$$

where $R_{sample}$ and $R_{standard}$ represent the value of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in the sample and the standard sample respectively. The measurement error of the instrument is $\delta^{2}H < 0.3$ ‰, $\delta^{18}O < 0.08$ ‰.

### Theoretical methods

In many regions, traditional methods of quantifying river flows are largely limited by the lack of long-term monitoring data. The isotope method can provide new insights for understanding the changed processes of river runoff and it can also be used as a practical tool to determine the contribution ratio of tributaries to mainstream at the confluence of rivers. Uhlenbrook *et al.* (2002) suggest that when using stable isotopes for hydrograph separation, it usually requires a common assumption that the water from different sources should have distinct isotopic compositions. The oxygen and hydrogen isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$) of precipitation, groundwater and surface water in the Tuojiang River catchment are usually different. Therefore, a simple $\delta^{18}O$ and $\delta^{2}H$ based binary model was used to determine the recharge source of groundwater and the contribution ratio of tributaries to the mainstream. When the model is applied to determine the groundwater recharge source, precipitation and river water are used as the two end members of groundwater recharge. When the model is applied to determine the contribution ratio of tributaries to the mainstream, the two rivers before their intersection are selected as the two end members. The model is defined as follows:

$$f_1 = \frac{C_2 - C_3}{C_2 - C_1} \tag{2}$$

$$f_2 = \frac{C_3 - C_1}{C_2 - C_1} \tag{3}$$

where $f_1$ is the fraction of component 1 in component 3, and $f_2$ is the fraction of component 2 in component 3. $C$ are isotopic concentrations, the subscript 3 represents the water source after the mixing, while 1 and 2 represent the two water sources before the mixing.

Assuming the uncertainty of each variable is independent of the uncertainty in others, the Gaussian error propagation technique is applied to estimate the uncertainty of the $f$ using the following equation (Genereux 1998):

$$W_f = \left[\sum_{i=1}^{n}\left(\frac{\partial f}{\partial Ci} W_{Ci}\right)^2\right]^{0.5} \tag{4}$$

where $f$ represents the contribution of a specific runoff component, and W is the uncertainty of the variable specified by the subscript.

The Tuojiang River flows through many industrial and densely populated areas, so water quality is greatly affected by human activities. Studying the *MRT* of Tuojiang River and its tributaries can provide important information for us to understand the catchment response to precipitation. This paper applies periodic regression analysis to fit the annual $\delta^{18}O$ seasonal sine wave curve for reflecting the seasonal variations of $\delta^{18}O$ in precipitation, Tuojiang River and its four tributaries (Yazi River, Shiting

River, Mianyuan River and Pihe River). The data is optimized by the least squares method. The definition is as follows (Rodgers *et al.* 2005):

$$\delta^{18}O = \mathrm{X} + \mathrm{A}[\cos(\mathrm{ct} - \theta)] \tag{5}$$

where $\delta^{18}O$ refers to the simulated $\delta^{18}O$, X refers to the annual average of the measured $\delta^{18}O$ value, A is the annual amplitude of the measured value $\delta^{18}O$, $c$ is the annual fluctuation of the radial frequency (0.017214 rad $\mathrm{d}^{-1}$), and t is the number of days between the sampling time and the starting time (2018/5/6); $\theta$ refers to the phase lag or time at which $\delta^{18}O$ peaks.

The *MRT* was estimated via an exponential model in which precipitation inputs are assumed to mix rapidly with resident water by the following equation (Małoszewski *et al.* 1983):

$$MRT = c^{-1}[(A_{Z2}/A_{Z1})^{-2} - 1]^{0.5} \tag{6}$$

In this equation, $A_{Z1}$ is the amplitude of rainfall, $A_{Z2}$ is the amplitude of river water and $c$ is the radial frequency of the annual amplitude of Equation (5).

The detailed process of each model can be seen as follows (Figure 3).

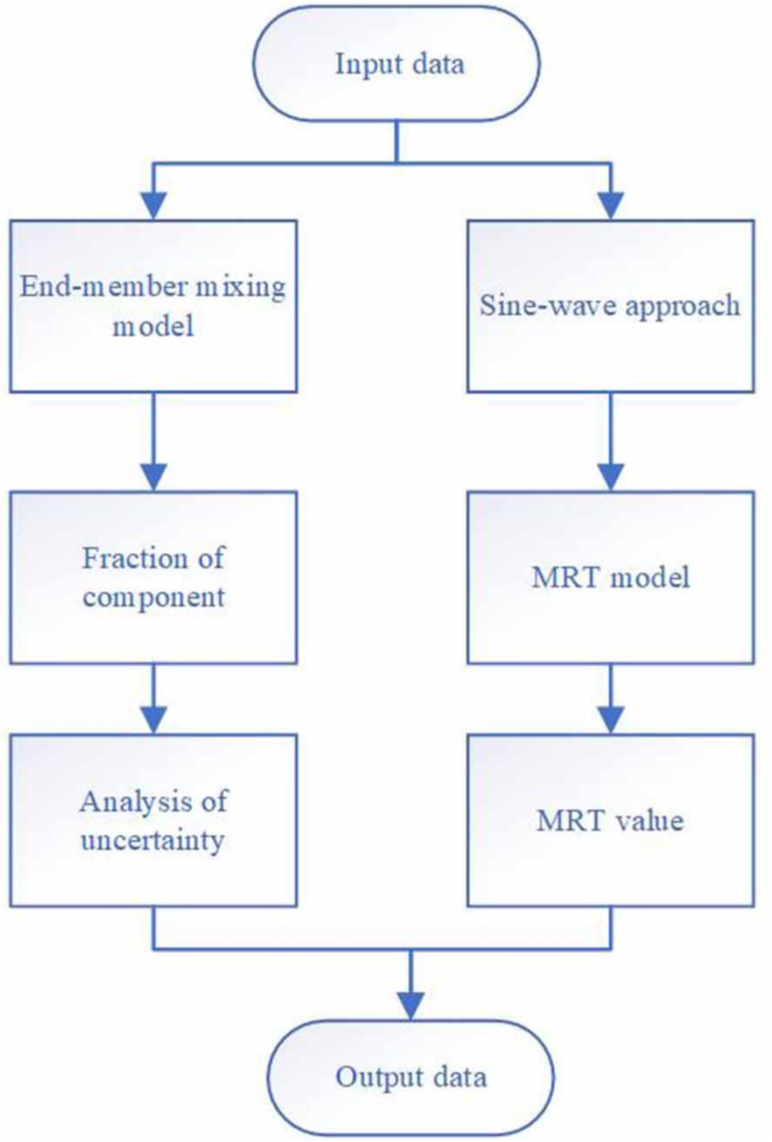

**Figure 3** | Flow chart of the end-member mixing model (left) and *MRT* model (right).

## RESULTS AND DISCUSSION

### Isotopic variation characteristics of precipitation, river water and groundwater

#### Isotopic variation characteristics of precipitation

Based on the stable isotope data of precipitation in Chengdu from May 2018 to April 2019, the temporal variations of $\delta^{18}O$ and $\delta^{2}H$ in precipitation are investigated. The isotopic composition of precipitation can be highly variable. The negative values for $\delta^{18}O$ and $\delta^{2}H$ are throughout the whole year and the *d-excess* value is positive. Isotopic contents range from −12.01 to −0.83 ‰ for $\delta^{18}O$, from −85.95 to −0.99 ‰ for $\delta^{2}H$ and from 7.42 to 22.28 ‰ for *d-excess*. Average values for the stable isotope in precipitation in the catchment are $\delta^{18}O = -6.45$ ‰, $\delta^{2}H = -38.93$ ‰ and *d-excess* = 13.35 ‰ (Table 2). A significant seasonal variation of the isotope in precipitation is observed. In the wet season (May to October), precipitation shows depleted isotopes and fluctuates greatly. In detail, the average $\delta^{18}O$, $\delta^{2}H$ and *d-excess* values of precipitation are −8.45 ‰, −56.49 ‰, and 11.14 ‰ respectively. Its isotope value decreases from May to July and increases from July to October. The extremely low $\delta^{18}O$ and $\delta^{2}H$ values are observed in July ($\delta^{18}O = -12.01$‰, $\delta^{2}H = -85.95$ ‰) (Figure 4). In the dry season (November to April), the isotope values gradually enrich from November to April and reach the maximum in February ($\delta^{18}O = -0.83$ ‰, $\delta^{2}H = -0.99$ ‰). The average $\delta^{18}O$, $\delta^{2}H$ and *d-excess* values of precipitation are −4.05 ‰, −17.85 ‰, and 15.56 ‰, respectively.

**Table 2** | Weighed mean and ranges of $\delta^{18}O$ and $\delta^{2}H$ values together with the estimated *MRT* in River Tuojiang catchment for the years 2018–2019

| Sample type | Category | Minimum | Maximum | Annual average | Mean value in wet season | Mean value in dry season | *MRT* (year) |
|---|---|---|---|---|---|---|---|
| Precipitation | $\delta^{2}H$ (‰) | – 85.95 | – 0.99 | – 38.93 | – 56.49 | – 17.85 | - |
| | $\delta^{18}O$ (‰) | – 12.01 | – 0.83 | – 6.45 | – 8.45 | – 4.05 | |
| | *d-excess* (‰) | 7.42 | 22.28 | 13.35 | 11.14 | 15.56 | |
| Groundwater | $\delta^{2}H$ (‰) | – 71.43 | – 43.93 | – 59.81 | – 58.63 | – 61.29 | - |
| | $\delta^{18}O$ (‰) | – 10.46 | – 6.12 | – 8.34 | – 8.18 | – 8.55 | |
| | *d-excess* (‰) | – 1.33 | 16.41 | 6.92 | 6.77 | 7.11 | |
| All river water | $\delta^{2}H$ (‰) | – 81.94 | – 46.81 | – 68.89 | – 68.57 | – 69.27 | 1.07 |
| | $\delta^{18}O$ (‰) | – 12.05 | – 6.37 | – 9.84 | – 9.77 | – 9.93 | |
| | *d-excess* (‰) | – 5.6 | 24.41 | 9.55 | 9.15 | 10.04 | |
| Yazi River | $\delta^{2}H$ (‰) | – 76.61 | – 61.46 | – 69.65 | – 69.3 | – 70.06 | 0.95 |
| | $\delta^{18}O$ (‰) | – 11.07 | – 8.78 | – 10.04 | – 9.96 | – 10.12 | |
| | *d-excess* (‰) | 6.25 | 17.23 | 10.43 | 10.02 | 10.93 | |
| Shiting River | $\delta^{2}H$ (‰) | – 72.71 | – 54.07 | – 65.38 | – 65.71 | – 64.98 | 1.03 |
| | $\delta^{18}O$ (‰) | – 10.24 | – 7.75 | – 9.35 | – 9.26 | – 9.45 | |
| | *d-excess* (‰) | 5.46 | 12.2 | 9.28 | 8.15 | 10.64 | |
| Mianyuan River | $\delta^{2}H$ (‰) | – 66.16 | – 53.86 | – 62.51 | – 62.08 | – 63.04 | 1.49 |
| | $\delta^{18}O$ (‰) | – 10.67 | – 7.39 | – 9.05 | – 8.96 | – 9.16 | |
| | *d-excess* (‰) | 5.23 | 20.58 | 9.87 | 9.55 | 10.26 | |
| Pihe River | $\delta^{2}H$ (‰) | – 81.94 | – 67.65 | – 76.3 | – 76.81 | – 75.68 | 1.35 |
| | $\delta^{18}O$ (‰) | – 12.05 | – 9.92 | – 10.84 | – 10.96 | – 10.69 | |
| | *d-excess* (‰) | 4.3 | 17.05 | 10.01 | 10.14 | 9.85 | |

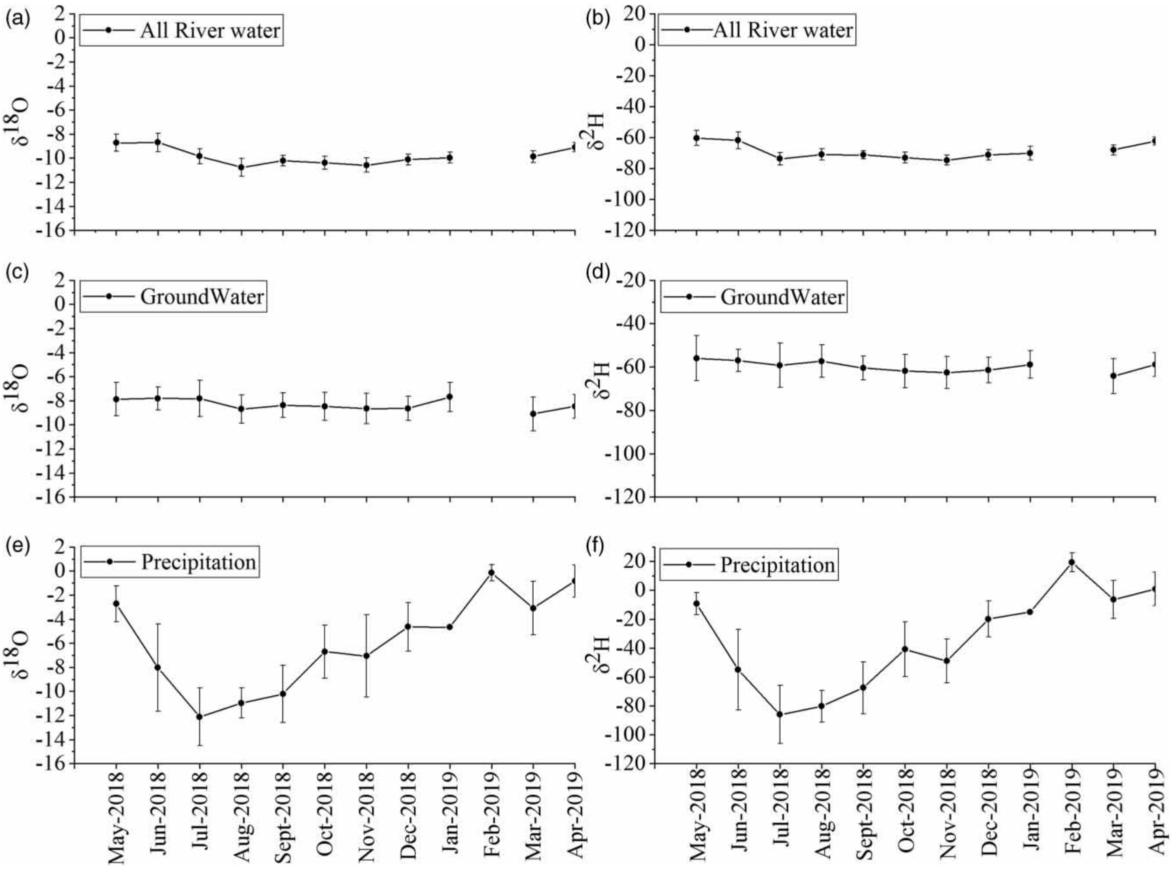

**Figure 4** | Temporal variations in $\delta^{18}O$ and $\delta^{2}H$ values of all river water ((a) and (b)), groundwater ((c) and (d)) and precipitation ((e) and (f)).

In the wet season, the isotope value of precipitation shows a wide variation range and obviously precipitation amount effect (i.e. isotope value shows a reverse trend with precipitation amount). This phenomenon is also observed in other regions in China and shows the same trend in the wet season (Ma *et al.* 2016; Wan *et al.* 2018). In this region, we found that extreme precipitation events are also reflected in the isotopic composition of precipitation. According to the record, the total precipitation amount is 556 mm in July. The extremely low $\delta^{18}O$ and $\delta^{2}H$ values in July may be related to the extremely high precipitation amount caused by the East Asian monsoon and Indian monsoon in Sichuan (Yu *et al.* 2017). In the dry season, the relative humidity is low with a decrease in precipitation amount. During the precipitation process, the rainwater is easily influenced by evaporation before reaching the ground. As a result, the isotope kinetic fractionation effect occurs and enriches the isotope values in precipitation. Another reason for the different isotope values in precipitation between $\delta^{18}O$ and $\delta^{2}H$ are the sources of water vapor. To prove that, the *d-excess*, which is affected by the relative humidity in the water vapor source area and could be used for indicating the source of water vapor (Jouzel & Merlivat 1984; Bershaw *et al.* 2020), is investigated. The d-excess value of precipitation in the dry season is higher than that in the wet season. Usually, the *d-excess* value is low in the water vapor from the low latitude ocean surface, which leads to a low *d-excess* value in the precipitation. On the contrary, water vapor from arid areas will lead to a high *d-excess* value in the precipitation (Shi *et al.* 2020). Chengdu belongs to the East Asian monsoon region where air masses are mainly derived from the low latitude ocean in the wet season. In the dry season, water vapor mainly comes from the arid inland areas in the west. This is consistent with the finding of other precipitation studies in Southwestern China (e.g. Zhang *et al.* 2008; Hu *et al.* 2018).

### Isotopic variation characteristics of river water from the mainstream of Tuojiang River and its tributary

In all river water, its isotope values show a medium variation range comparable to that of precipitation and groundwater. Specifically, the annual $\delta^{18}O$, $\delta^{2}H$ and *d-excess* values in all river water vary from −12.06 to −6.37 ‰, −81.94 to −46.81 ‰ and −5.62 to 24.41 ‰ respectively. The temporal variation in $\delta^{18}O$ and $\delta^{2}H$ of all river water also show a similar season variation like that in precipitation (Figure 4). The isotopic composition of river water decreased from May 2018 to August 2018 and increased from September 2018 to April 2019. This variation indicates river water in the Tuojiang river catchment is recharged by precipitation and the isotopic characteristics of precipitation are inherited. In the wet season, the average $\delta^{18}O$, $\delta^{2}H$ and *d-excess* values of all river waters are −9.77 ‰, −68.65 ‰, and 9.15 ‰ respectively. The $\delta^{18}O$ and $\delta^{2}H$ values of all river waters in the wet season are larger than those of river water in the dry season. This variation is in contrast to our expectation that the isotope-depleted precipitation input to river water will lead to lower $\delta^{18}O$ and $\delta^{2}H$ value of river water in the wet season than that of the dry season. The possible reason is that in Tuojiang River Basin, the river mainly receives more isotope-depleted groundwater in the dry season, which leads to the depleted isotope value of river water relative to that of the wet season. By comparing the isotope value between river water and groundwater (Figure 4), it can be found that the isotopic composition of river water in winter (December to February) is close to that of groundwater in autumn (September to November). It is indicated that the groundwater stored in autumn recharges river water in winter. The variation in the isotopic composition of river water collected from four tributaries are investigated (Table 1 and Figure 5).

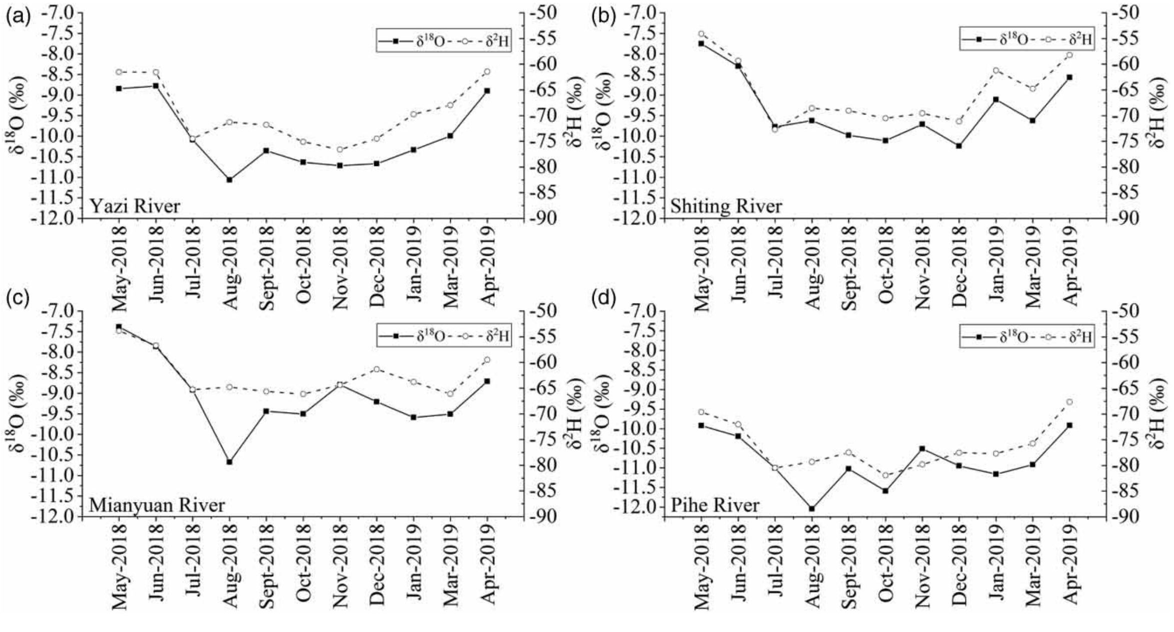

**Figure 5** | Temporal variations in $\delta^{18}O$ and $\delta^{2}H$ of the Yazi River (a), Shiting River (b), Mianyuan River (c) and Pihe River (d).

Among the four tributaries of Tuojiang River, the average $\delta^{18}O$ and $\delta^{2}H$ values are in the order of the Mianyuan River (−9.05 ‰, −62.51 ‰) > Shiting River (−9.35 ‰, −65.38 ‰) > Yazi River (−10.04 ‰, −69.65 ‰) > Pihe River (−10.84 ‰, −76.3 ‰). In August 2018, an increasing trend in $\delta^{2}H$ values of four river waters is observed, but $\delta^{18}O$ values show a decreasing trend in Yazi River, Mianyuan River and Pihe River. However, the increasing $\delta^{18}O$ and $\delta^{2}H$ values of precipitation are observed in August compared with the previous month. It indicates that the opposite trends of stable isotope measurements of oxygen and hydrogen in river water are not the result of precipitation input but the replenishment effect of depleted-isotope ice and snow meltwater. Because of the influence of equilibrium fractionation and kinetic fractionation at low temperature, the ice-snow meltwater contains a relatively depleted $\delta^{18}O$ value and enriched $\delta^{2}H$ value. Glacier water and snowmelt amount reach the annual peak in August at the headwater area, while the precipitation is significantly lower than that in July. The increase in the supply ratio of ice-snow meltwater to the river leads to the isotopic fingerprint of the ice-snow meltwater being observed in the downstream river water. The same phenomena are also found in the study of the Hailuogou river (Meng & Liu 2018) and the mountainous Bringi catchment of Kashmir Himalaya (Bhat & Jeelani 2018). In the Tuojiang River Basin, the $\delta^{18}O$ *and* $\delta^{2}H$ values of river water fluctuate along the river but are enriched generally. Generally, the source of the river is in the mountainous area. Affected by the precipitation amount effect and temperature effect as it has a high rainfall and low temperature, the isotope value of the upstream river water is low. Instead, in the downstream of the river, the isotope value of the river water increases along the river due to the evaporation enrichment effect (Ogrinc *et al.* 2008; Zhao & Li 2017). The decrease in $\delta^{18}O$ and $\delta^{2}H$ values are due to the inflow of the Minjiang River into the Tuojiang River (Wu *et al.* 2020) (Figure 6). The study of the Heishui River in the upper reaches of the Minjiang River shows that even in the rainy season, the main supply source of the Minjiang River water is meltwater. So the isotope values of Minjiang River water are generally depleted compared with those of Tuojiang River (Liu *et al.* 2008). Moreover, S2, S4 and T4 are river junctions, affected by the inflow of isotope-depleted river water, the isotope values of the river water decrease after the junctions.

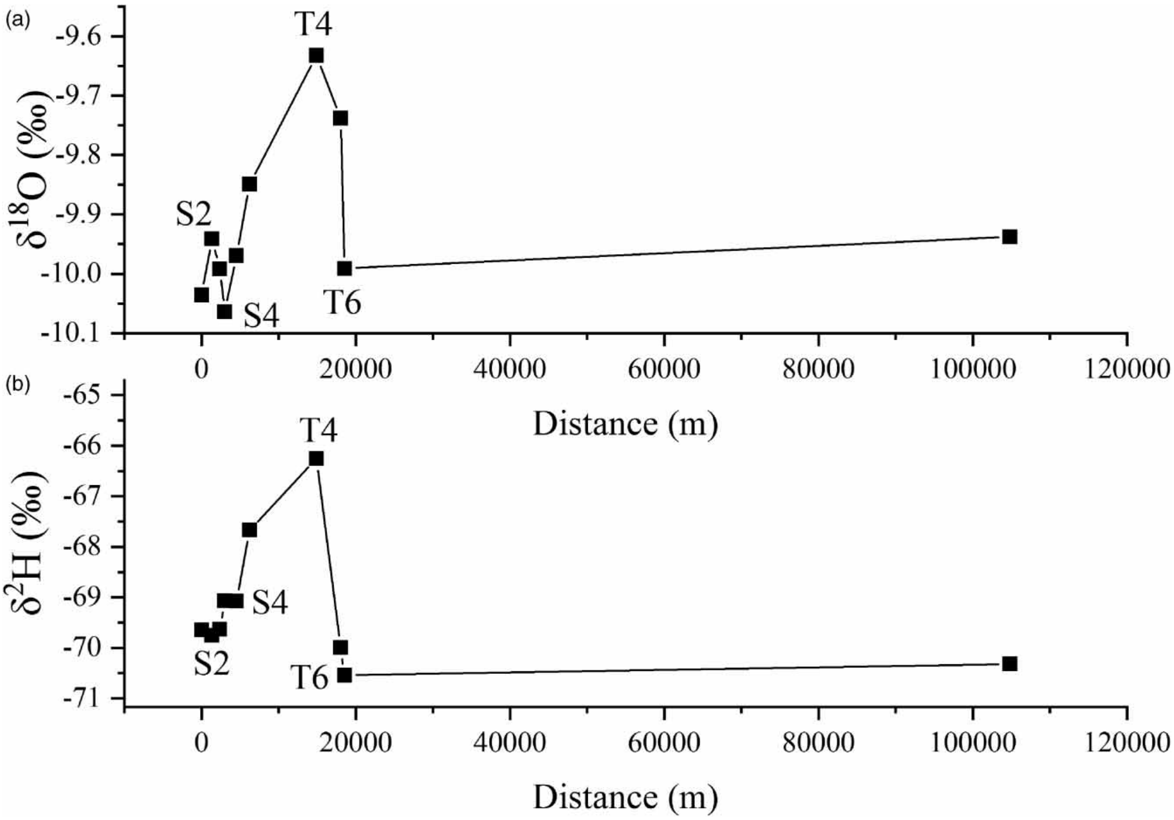

**Figure 6** | Spatial variations in $\delta^{18}O$ and $\delta^{2}H$ along the Tuojiang River (S2, S4, T4, T6 are located at the junction of the principal river courses and its tributaries).

### Isotopic variation characteristics of groundwater

The groundwater from the upper reaches of the Tuojiang River contains a relatively small magnitude of variations. Its $\delta^{18}O$, $\delta^{2}H$ and *d-excess* values range from −10.46 to −6.12 ‰ for $\delta^{18}O$, from −71.43

to −43.93 ‰ for $\delta^2H$ and from −16.41 to 1.33 ‰ for *d-excess*. The average values of $\delta^{18}O$, $\delta^2H$ and *d-excess* are −8.34 ‰, −59.81 ‰, −6.92 ‰, respectively. In the wet season, the average values of $\delta^{18}O$, $\delta^2H$ and *d-excess* are −8.18 ‰, −58.63 ‰ and −6.77 ‰, compared with the values of −8.55 ‰, −61.29 ‰ and −7.11 ‰ in the dry season, respectively. The isotope value of groundwater is enriched in the wet season and depleted in the dry season, and it is enriched compared with the river water in the same period (Table 2). The average value of $\delta^{18}O$ in the wet season is only 0.37 ‰ away from the dry season, which suggests that the groundwater is relatively stable between the wet season and dry season, resulting from the long-term recharge of surface water and precipitation. The isotope variation ranges of groundwater ($\delta^{18}O$ are −10.46 to −6.12‰ and $\delta^2H$ are −71.43 to −43.93 ‰ *)* is within the range of river water ($\delta^{18}O$ are −12.06 to −6.37 ‰ and $\delta^2H$ are −81.94 to −46.81 ‰) and precipitation ($\delta^{18}O$ are −12.01 to −0.83 ‰ and $\delta^2H$ are −85.95 to −0.99 ‰). Its temporal variation trend is basically the same as that of precipitation and river water, indicating that groundwater is recharged by precipitation and river water simultaneously. The relatively small isotope variations of groundwater reflect the retention effect of groundwater, which is not obvious over time. Comparing Figure 4 (a)–4(d), it can be seen that the isotopic composition of groundwater throughout the year is very nearly to that of river water. This phenomenon indicates that the groundwater may exchange frequently with river water and the river water is the major recharge source of groundwater rather than precipitation. The well we collected groundwater sample is close to the river bank. In this region, there are close hydraulic relations between groundwater and river water. The isotopic composition of groundwater and river water provides evidence for this close hydraulic relation (Shamsuddin *et al.* 2018). This close hydraulic relationship among groundwater and river water will be weak with the increase in the distance to the river (Zhao & Li 2017; Kong *et al.* 2018).

## Relationship between $\delta^2$H and $\delta^{18}$O in different water cycle components

Craig (1961) found a linear relationship between $\delta^{18}O$ and $\delta^2H$ in precipitation by analyzing the stable isotopic compositions of oxygen and hydrogen in different water bodies around the world and proposed a global meteoric water line equation (GMWL): $\delta^2H = 8\delta^{18}O + 10$. According to the Rayleigh fractionation model, stable isotopes of hydrogen and oxygen in water are enriched and depleted in the process of water distillation. The kinetic effect in fast evaporation can disturb the above-mentioned parallelism between the $\delta^{18}O$ and $\delta^2H$ variations, resulting in different relationships between $\delta^{18}O$ and $\delta^2H$ values of precipitation in different regions (i.e. the slope and intercept of the local meteoric water line (LMWL) are different). For example, Lide & Yao (2001) obtained LMWL from north to south Delingha, Tuotuohe and Lhasa on the Tibet Plateau, in which $\delta^2H = 8.47\delta^{18}O + 15.2$ ($R^2 = 0.98$), $\delta^2H = 8.21\delta^{18}O + 17.46$ ($R^2 = 0.967$), $\delta^2H = 7.90\delta^{18}O + 6.29$ ($R^2 = 0.97$). Ansari *et al.* (2020) obtained the LMWL of Mumbai which is given by $\delta^2H = (8.90 \pm 0.5)\ \delta^{18}O + (10.5 \pm 0.9)$ ($r = 0.95$). Based on the weighted average $\delta^{18}O$ and $\delta^2H$ values of monthly precipitation during the study period, the LMWL equation in Chengdu is calculated as $\delta^2H = 8.394\delta^{18}O + 15.3$ ($R^2 = 0.98$, $P < 0.01$). Its slope and intercept are slightly larger than the GMWL. This may be attributed to the fact that Chengdu belongs to the Sichuan Basin, with an annual rainfall of 1,000 mm–1,300 mm and low evaporation. Most of the precipitation is concentrate in the wet season and the meteoric water line equation for the wet season is $\delta^2H = 8.2522\delta^{18}O + 13.277$ ($R^2 = 0.99$, $P < 0.01$), which is closer to the slope and intercept of the GMWL. The meteoric water line equation for the dry season is $\delta^2H = 7.8157\delta^{18}O + 13.837$ ($R^2 = 0.879$, $P < 0.01$). Its slope and intercept are smaller than those of the rainy season and the LMWL (Figure 7).

This can be attributed to the low rainfall and relative humidity in the dry season. The influence of isotope non-equilibrium fractionation is caused by secondary evaporation of raindrops during the falling process, resulting in relative deleption of $\delta^2H$ and relative enrichment of $\delta^{18}O$ in precipitation (Meng Yuchuan 2010; Crawford *et al.* 2017). According to the oxygen and hydrogen isotopic

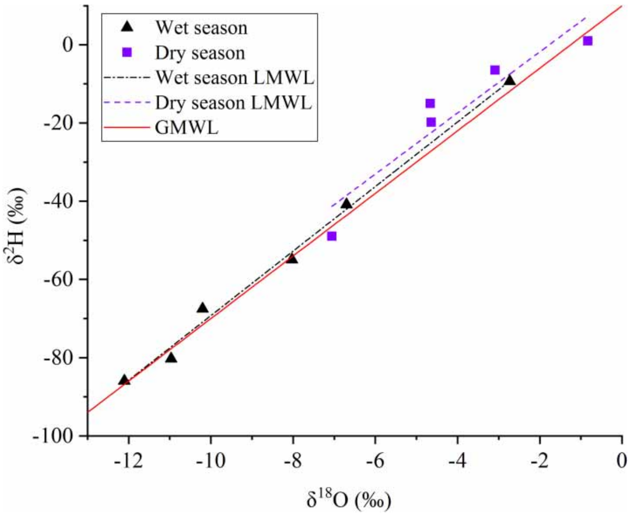

**Figure 7** | Relationship between $\delta^2H$ and $\delta^{18}O$ values for precipitation during the wet season (triangle) and dry season (square).

composition ($\delta^{18}O$ and $\delta^2H$) of groundwater and river water during the study period, the linear regression analysis of $\delta^{18}O$ and $\delta^2H$ values are carried out to obtain the groundwater line (GL) of groundwater in $\delta^2H$ and $\delta^{18}O$ (Figure 8):

$$\text{Year – round GL:}\delta^2H = 5.7634\delta^{18}O - 11.738(\mathrm{R}^2 = 0.88,\ \mathrm{P} < 0.01); \tag{7}$$

$$\text{GL in wet season:}\delta^2H = 5.9617\delta^{18}O - 9.8958(\mathrm{R}^2 = 0.84,\ \mathrm{P} < 0.01); \tag{8}$$

$$\text{GL in dry season:}\delta^2H = 5.4216\delta^{18}O - 14.938(\mathrm{R}^2 = 0.94,\ \mathrm{P} < 0.01); \tag{9}$$

The equation of the relationship between $\delta^2H$ and $\delta^{18}O$ in river water (river line, RL) is:

$$\text{Year-round SL:}\delta^2H = 6.0225\delta^{18}O - 9.6352(\mathrm{R}^2 = 0.76,\ \mathrm{P} < 0.01); \tag{10}$$

$$\text{RL in wet season:}\delta^2H = 5.5811\delta^{18}O - 14.068(\mathrm{R}^2 = 0.73,\ \mathrm{P} < 0.01); \tag{11}$$

$$\text{RL in dry season:}\delta^2H = 7.2604\delta^{18}O + 2.8247(\mathrm{R}^2 = 0.86,\ \mathrm{P} < 0.01); \tag{12}$$

Most of the isotopic data collected from groundwater are located between the LMWL and river line (RL) (Figure 8), which indicates that groundwater is mainly recharged by river and precipitation throughout the year. The intersection of the RL and the LMWL can reveal the average isotopic composition of the precipitation entering the river. According to the intersection points of the SL in the wet season and LMWL, and the intersection points of the SL in the dry season and the LMWL, it is found that the $\delta^{18}O$ and $\delta^2H$ values at the intersection points are close to the $\delta^{18}O$ and $\delta^2H$ values of precipitation in July, August and September. It indicates that most of the river water in both wet and dry season comes from the precipitation in July, August and September. Precipitation has a seasonal lag in the recharge of the river. The precipitation in the wet season is divided into two parts, one part is directly transferred into the river through the overland flow, and the other part is stored in a shallow aquifer by interflow. On the seasonal scale, the GL in the wet season lies between the LMWL and the RL in the wet season and the slope of the GL in the wet season is close to that of the wet season RL. It indicates that the groundwater is mainly recharged by the river water during the wet season. The slope of the GL during the dry season is close to that of the wet season and the slope of the RL in the wet season is relatively larger than the slope of GL in the dry season. It suggests that the groundwater in both the dry season and wet season mainly comes from the replenishment of river water during the wet season and has experienced evaporation to some extent.

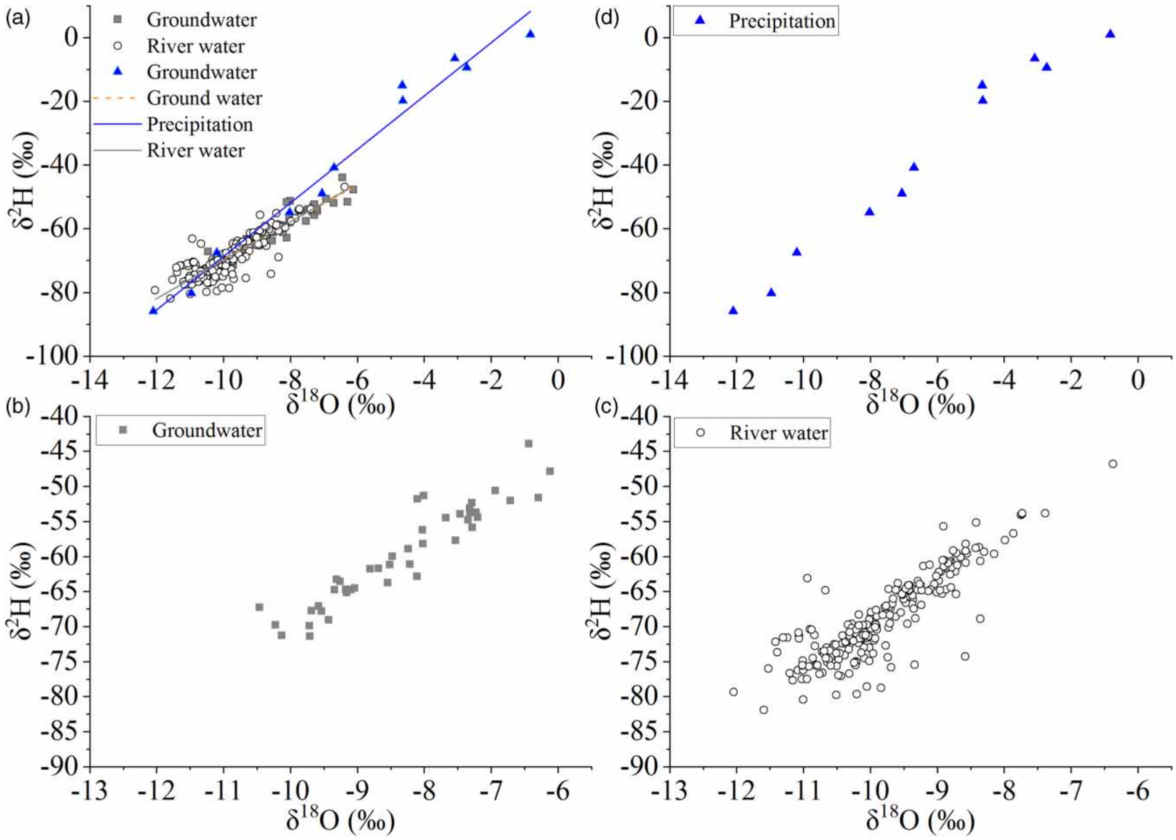

**Figure 8** | Correlation between $\delta^{2}H$ and $\delta^{18}O$ values for waters collected in Tuojiang watershed from May 2018 to November 2019: (a) all water samples, (b) precipitation, (c) groundwater, (d) river water. (a) The local meteoric water line (LMWL) and river line (SL) is shown as a solid line. For comparison, the groundwater line (GL) is shown as a dashed line.

## Interactions between precipitation, river water and groundwater

The Tuojiang River catchment has developed industries and frequent irrigation activities, so there is a large demand for water resources. There are close hydraulic relations among precipitation, river water, and groundwater. Quantifying the process of precipitation and river water recharge to groundwater in different periods is important to manage and utilize water resources in the catchment. However, the interactions among precipitation, river water and groundwater in the upper reaches of the Tuojiang River have not been investigated in detail in previous studies. The isotope value and GL of groundwater are both between those of precipitation and river water, indicating that groundwater is recharged by precipitation and river water together. Then, seasonal changes in groundwater sources are further calculated based on $\delta^{2}H$ and $\delta^{18}$O data (Table 3).

**Table 3** | The proportion of precipitation and river water recharge to groundwater in different seasons and its uncertainty in the upper River Tuojiang

| Season | Spring | | Summer | | Autumn | | | Winter | |
|---|---|---|---|---|---|---|---|---|---|
| | $^{2}$H | $^{18}$O | $^{2}$H | $^{18}$O | $^{2}$H | $^{18}$O | | $^{2}$H | $^{18}$O |
| River | 67.7 (%) | 62.1 (%) | 43.8 (%) | 14.7 (%) | 65.7 (%) | 47 (%) | Groundwater in Autumn | 99.8 (%) | 98.5 (%) |
| Precipitation | 32.3 (%) | 37.9 (%) | 56.2 (%) | 85.3 (%) | 34.3 (%) | 53 (%) | Precipitation | 0.2 (%) | 1.5 (%) |
| $W_f$ | 0.7 (%) | 1.7 (%) | 1.1 (%) | 2.7 (%) | 0.7 (%) | 1.7 (%) | | 0.7 (%) | 1.5 (%) |

In spring and autumn, results calculated by $\delta^2H$ and $\delta^{18}$O both show the recharge from river water is higher than precipitation. In Spring, the temperature rises lead to the melting of snow and ice in the headwater region. This increases the amount of water coming from upstream of the river, thus leads to the increase of the lateral recharge from river water to the groundwater. A similar recharge ratio of precipitation and river water to groundwater is observed between spring and autumn. This is because of the precipitation amount in the Tuojiang River region during the spring (March to May) and autumn (June to April). In autumn, the results calculated by $^{18}$O and $^2$H are beyond our expectation that a different trend is observed in oxygen and hydrogen isotopes. Autumn is the season of rice maturity, local residences pump well or river water for irrigation. During this process, the evaporation of water ponded after irrigation increases, resulting in non-equilibrium fractionation. The concentrations of $^{18}$O and $^2$H in water change to different degrees. The distinct variation trend between $\delta^2H$ and $\delta^{18}$O in groundwater from August to October proved this process. In summer, the recharge ratio of precipitation to groundwater increases significantly and surpasses the river water. Influenced by the water vapor transported by the southwest and southeast monsoon, the precipitation amount and frequency increase significantly. Heavy precipitation falls on the catchment and recharges the groundwater by interflow. During the winter, because of the influence of Mongolia High, this region is controlled by the dry cold terrigenous water vapor carried by the inland monsoon. The precipitation amount and temperature decrease, which results in decreasing precipitation and meltwater from the upstream. As a result, the value of the river stage reduces. When the river level is lower than the adjacent groundwater level, the groundwater no longer accepts the supply from the river. Groundwater in winter mainly consists of two components, namely groundwater stored in Autumn and replenishment of precipitation in winter. This result is contrary to the conclusion that the groundwater in the Pihe River still accepts river water during winter (Chen *et al.* 2020b). This is because of the existence of the Dujiangyan Irrigation Project in the upper reaches of the Pihe river. This regulates the water resource of the Pihe River, thus maintaining the river level. In the whole year, the fraction of precipitation recharge to groundwater is consistent with the variation trend of the precipitation amount. It means that the groundwater responds harmoniously to precipitation in the upper reaches of Tuojiang River. The fraction of river water recharge to groundwater is significant all year round except for winter. In winter, because the Tuojiang River water significantly decreases and its pollutant discharge, the concentration of organic matter is seriously over standard. Rational use of groundwater to recharge river water may help to relieve the pollution problem in the Tuojiang River. Given the uncertainty in measure $\delta^2H$ and $\delta^{18}$O concentrations, we calculate how this uncertainty is propagated into our result by using Equation 4. The result (Table 3) shows the uncertainty $W_f$ is small and cannot affect the accuracy of our calculated result. Comparing the $W_f$ of $\delta^2H$ and $\delta^{18}$O, it can be seen that the uncertainty of $\delta^{18}$O is higher than $\delta^2H$, though both are small. This may indicate that using the end-member mixing model by $\delta^2H$ will obtain a more accurate result. Compared to the results of other studies (Meng & Liu 2016; Chen *et al.* 2020b) using the same model in southwest China, the result shows a similar trend. Distinct isotopic compositions of precipitation, river water, and groundwater are observed and it is possible to use the end-member mixing model based on isotope data. The results all show the same variation trend with precipitation and different variation trends between the wet and dry season. This indicates that precipitation shows strong seasonal variation in southwest China and this variation will also be reflected in other water bodies like groundwater and river water.

### Hydrograph separation of Tuojiang River

To better understand the seasonal variations in the water sources of the Tuojiang River, a dual-end member mixing model based on $^2$H data is used in each section to calculate quantitatively the contribution rate of each tributary volume over the total river. The results show that in the spring, the contribution rate of the tributaries to the Tuojiang River is in the order of Pihe (65.6%) > Yazi

River (21.3%) > Shiting River (7.5%) > Mianyuan River (5.6%). In summer, the order of contribution rate of each tributary to the Tuojiang River is Pihe River (63.8%) > Yazi River (20.2%) > Mianyuan River (12.7%) > Shiting River (3.3%). In autumn, the order is Pihe River (43.4%) > Mianyuan River (29.3%) > Shiting River (17.4%) > Yazi River (9.9%). In winter, the contribution rate of the Yazi River and Shiting River is less than zero (Table 4).

**Table 4** | The contribution rate of the Yazi River, Shiting River, Mianyuan River and Pihe River to the water volume of the Tuojiang River

| Season | Yazi River | Shiting River | Mianyuan River | Pihe River |
|---|---|---|---|---|
| Spring | 21.3% | 7.5% | 5.6% | 65.6% |
| Summer | 20.2% | 3.3% | 12.7% | 63.8% |
| Autumn | 9.9% | 17.4% | 29.3% | 43.4% |
| Winter | 0 | 0 | 54.5% | 45.5% |

This is because the water quantity before and after the river confluence is assumed to be in balance and fully mixed when using the end-member mixing model. However, this assumption is not completely accurate for most rivers due to the difference in water flow conditions, which brings about deviation from the actual situation. The division ratio can't be negative, so the calculation result of winter is taken as zero here. Therefore, the Mianyuan River and Pihe River contribute 54.5% and 45.5% to Tuojiang River in winter, respectively. Among the four tributaries of the Tuojiang River, the Pihe River has the largest contribution rate to the Tuojiang River, and the ratio is higher in spring and summer, lower in autumn and winter. The Shiting River contributes the least to the Tuojiang River. Its minimum value is only 3.28% in summer, but its contribution in autumn is more significant. The contribution rate of the Mianyuan River to Tuojiang River water volume varies significantly throughout the year. The contribution ratio of the Mianyuan River is small in spring and summer, while the contribution ratio is large in autumn and winter. The contribution of the Yazi River to Tuojiang River is relatively stable among the three seasons of the year. These results indicate that the Mianyuan River and Pihe River have a higher contribution rate to the entire Tuojiang River. Compared to the Mianyuan River, the variation in contribution ratio of the Pihe River to the Tuojiang River is stable. The reason is the regulating effect of the existence of the Dujiangyan Irrigation Project in the upper reaches of the Pihe river. This indicates that the water conservancy project is useful to manage the water resource in the river. The Tuojiang River is a river with serious pollution problems and its water resource shortage is severe = in dry winters. Thus, building a water conservancy project is an effective measure to maintain the river level in the dry season and relieve the pollution problem.

### Mean residence time of the Tuojiang River and its tributaries

*MRT* is a basic descriptor for the basin, which reflects the water storage capacity, flow path and water source information. The *MRT* value is directly related to the internal process of the basin. The distribution of the *MRT* describes how the watershed maintains and releases water and solutes, thus controlling the biogeochemical cycle and the migration of pollutants. Therefore, it is important to study *MRT* for water resources management and environmental protection in the basin (Sivapalan 2003). In this study, $\delta^{18}O$ seasonal trends in precipitation and river water can be qualitatively used to fit seasonal sinusoidal waves to simulate annual $\delta^{18}O$ changes in the river water and precipitation. During the sample period, the model $A_{z1} = 5.577$ ‰ described the precipitation data well ($R^2 = 0.54$). The simulated $\delta^{18}O$ values of river water are well described in the Mianyuan River ($R^2 = 0.33$) and

Pihe River ($R^2 = 0.32$). Especially in Tuojiang River mainstream ($R^2 = 0.46$), Yazi River ($R^2 = 0.56$) and Shiting River ($R^2 = 0.47$), the simulated $\delta^{18}O$ values of river water have a good correlation with actual values (Figure 9).

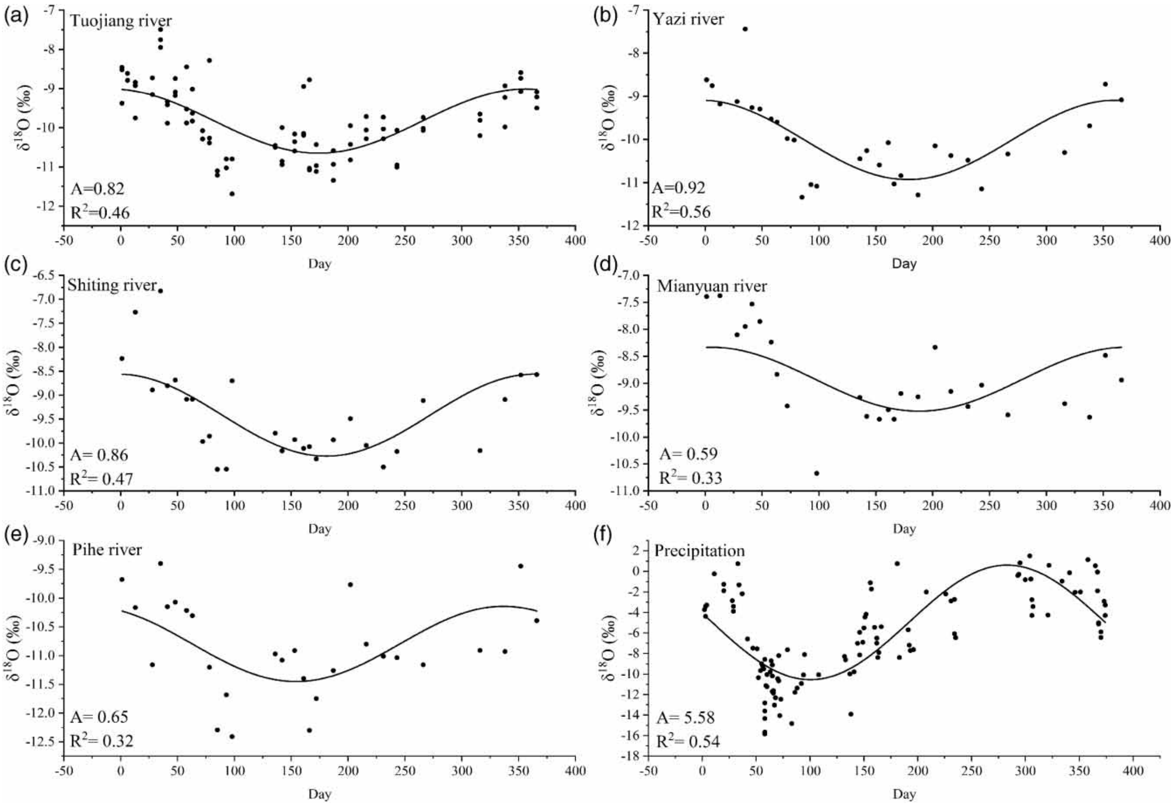

**Figure 9** | Annual regression models to $\delta^{18}O$ for precipitation, and surface water of the mainstream and tributaries of the upper Tuojiang River.

The estimated annual amplitude of simulated $\delta^{18}O$ in river water is lower than that of precipitation. The results of these simulations are then converted to an estimate of the water *MRT* by Equation (6). The *MRT* of the Tuojiang River is estimated to be 1.07 years, which is similar to the *MRT* of the Shiting River (1.02 years) and Yazi River (0.92 years). While the *MRT* of Mianyuan River and Pihe River are relatively long, with estimated values of 1.49 years and 1.35 years respectively (Table 2). The $\delta^{18}O$ value of river water is mainly controlled by the seasonal rainstorm runoff (freshwater) and stable groundwater (older water). So *MRT* can indicate the mixing degree of different sources, thus providing a valuable overall assessment of the differences in runoff processes in the Tuojiang River Basin as well as the management and regulation of water resources in the Tuojiang River. The *MRT* can also reflect the storage volumes of basin reservoirs to some extent. In the areas with low groundwater storage, the *MRT* is usually shorter (Małoszewski *et al.* 1983). The *MRT* of the Tuojiang River mainstream is 1.07 years, which is relatively short, indicating that there is not much groundwater storage in the basin. This can be attributed to the fact that the type of groundwater in the Tuojiang River Basin is mainly loose rock pore water. Its aquifer lithology is mainly gravel pebbles and silt pebbles, with strong permeability, small thickness and average water yield. *MRT* of each tributary of Tuojiang River varies greatly, ranging from 0.95 to 1.49 years. The *MRT* difference of these tributaries is due to the influence of topographical, geological and soil conditions and other factors. For example, Dewalle *et al.* (1997) compared the hydrological characteristics of two forest watersheds, West Virginia (WV 34–39 hectares) and Pennsylvania (PA 1134 hectares). Then, Dewalle *et al.* (1997) found that the mean transportation time of the base flow is longer for watersheds with smaller slopes. Rodgers *et al.* (2005) found that in the Feshie River Basin of the Cairngorm Mountains in Scotland, the *MRT* values are shorter in the headwater area covered with peat and shallow plateau soils, while longer *MRT* is observed in other tributaries with free-draining soil on the surface and larger groundwater storage in shallow aquifers. Along the flow path of Tuojiang River, the *MRT* of each tributary is gradually increasing, with the order of Yazi River < Shitingjiang < Pihe River < Mianyuan River. This result is in contrast to the result found in the Mandava catchment (Soulsby *et al.* 2010). The upper reaches of Tuojiang River Basin have steep slopes in mountain areas, while the middle reaches are described as gentle plain. Considering the cumulative effect of aquifers along the river flow path and the existence of older groundwater recharge, the *MRT* values of tributaries from the upper reaches to the lower reaches show an increasing trend. The shortest *MRT* is 0.95 years in Yazi River, where the $\delta^{18}O$ annual variation reaches the largest with a lower annual average $\delta^{18}O$ value. The shortest *MRT* and the close isotope value between Yazi River and precipitation both reflect that the Yazi River is greatly affected by rainfall. The *MRT* of Shiting River is relatively short, which could be attributed to more middle and upper Pleistocene peat cover in this basin, which makes it respond quickly to the input of precipitation. Moreover, after a storm, runoff can carry large amounts of pollutants into the river, causing the deterioration of river water quality. Therefore, when designating environmental protection, we should pay attention to the sensitivities of the two rivers, Shiting River and Yazi River, to pollutants. The *MRT* of Pihe River and Mianyuan River are both long. A long *MRT* means that the input of rainfall takes a long time to flow into the river channel through the watershed, which also means that rainfall has a longer biochemical reaction time with the river basin (Burns *et al.* 2003). On the other hand, the Pihe River and Mianyuan River contribute a large proportion to the water volume of the Tuojiang River. Therefore, we should conduct a water resources plan and environmental protection management according to the specific conditions of different tributaries of the Tuojiang River.

## CONCLUSIONS

- Isotopic composition of precipitation, groundwater, and river water show strong seasonal variation, enriching in the dry season and depleting in the wet season. Isotope variation between wet and dry season reflect the different water vapor source in the different seasons. Extreme precipitation events can be reflected in the isotopic composition of precipitation. The $\delta^{18}O$ and $\delta^{2}H$ values of the tributaries of the Tuojiang River are in the order of the Mianyuan River > Shiting River > Yazi River > Pihe River. Along the flow path, the isotope value of river water is gradually enriched and fluctuates in the river junction.
- Compared with the local meteoric water line in the wet season, the slope of the dry season is small, which indicates the precipitation in the dry season is affected by evaporation. The intersection of the RL and the LMWL indicated the majority of river water in the wet and dry seasons both come from the precipitation in July, August and September.
- Based on the isotopic composition of river water and precipitation, the relative contribution of river water and precipitation to groundwater is calculated. The results show that river water is the main source of groundwater and precipitation is the auxiliary source of groundwater throughout the year. In winter, groundwater receives little external recharge. Groundwater replenishes river water, which plays an important role in maintaining river stability and meeting ecological water demand. Therefore, we should be rational in development and employment of groundwater in the upper reaches of the Tuojiang River, especially in winter.
- The contribution of the tributaries to Tuojiang River water volume varies significantly with different space and time. The contribution of the Pihe River is the largest, reaching 65.6% and 63.8% in spring and summer, respectively, while that of the Shiting River is the smallest.

- The *MRT* of the Tuojiang River, Yazi River, Shiting River, Mianyuan River and Pihe River are 1.09, 0.95, 1.03, 1.49 and 1.35 years, respectively. The *MRT* of the river is both controlled by groundwater (older water) and precipitation (freshwater), thus the shorter *MRT* of the Tuojiang River Basin indicates that the groundwater storage is relatively low in Tuojiang River Basin. The *MRT* of the Yazi River and Shiting River is relatively small compared to other tributaries. Therefore, these two rivers respond quickly to rainfall, which makes it easy for a large number of pollutants to flow into the river and thus threatens the water environment. This study further proves the usefulness that the hydrological characteristics can be investigated and the environmental sensitivity can be evaluated by using stable isotopes even in a medium catchment with a complex source. It also provides a valuable application for calculating *MRT* by stable isotope in a medium catchment.

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## DATA AVAILABILITY STATEMENT

Data cannot be made publicly available readers should contact the corresponding author for details.

## REFERENCES

Ansari, M. A., Noble, J., Deodhar, A., Mendhekar, G. N. & Jahan, D. 2020 Stable isotopic ($\delta$18O and $\delta$2H) and geospatial approach for evaluating extreme rainfall events. *Global and Planetary Change* **194**, 103299.

Banks, E. W., Simmons, C. T., Love, A. J. & Shand, P. 2011 Assessing spatial and temporal connectivity between surface water and groundwater in a regional catchment: implications for regional scale water quantity and quality. *Journal of Hydrology* **404**(1–2), 30–49.

Bershaw, J., Hansen, D. D. & Schauer, A. J. 2020 Deuterium excess and 17O-excess variability in meteoric water across the Pacific Northwest, USA. *Tellus B: Chemical and Physical Meteorology* **72**(1), 1–17.

Bhat, N. A. & Jeelani, G. 2018 Quantification of groundwater–surface water interactions using environmental isotopes: a case study of Bringi Watershed, Kashmir Himalayas, India. *Journal of Earth System Science* **127**, 1–11.

Biggs, T. W., Lai, C.-T., Chandan, P., Lee, R. M., Messina, A., Lesher, R. S. & Khatoon, N. 2015 Evaporative fractions and elevation effects on stable isotopes of high elevation lakes and streams in arid western Himalaya. *Journal of Hydrology* **522**, 239–249.

Brooks, J. R., Gibson, J. J., Birks, S. J., Weber, M. H., Rodecap, K. D. & Stoddard, J. L. 2014 Stable isotope estimates of evaporation: inflow and water residence time for lakes across the United States as a tool for national lake water quality assessments. *Limnology and Oceanography* **59**(6), 2150–2165.

Burns, D. A., Plummer, L. N., McDonnell, J. J. & Busenberg, E. 2003 The geochemical evolution of riparian groundwater in a forested Piedmont catchment. *Ground Water* **41**(7), 913–925.

Chen, Q., Huang, M. & Tang, X. 2020a Eutrophication assessment of seasonal urban lakes in China Yangtze River Basin using Landsat 8-derived Forel-Ule index: a six-year (2013–2018) observation. *Science of the Total Environment* **745**, 135392.

Chen, K., Meng, Y., Liu, G., Xia, C., Zhou, J. & Li, H. 2020b Identifying hydrological conditions of the Pihe River catchment in the Chengdu Plain based on spatio-temporal distribution of $^{2}$H and $^{18}$O. *Journal of Radioanalytical and Nuclear Chemistry* **324**(3), 1125–1140.

Craig 1961 Isotopic variations in meteoric waters. *Science* **133**, 1702–1703.

Crawford, J., Hollins, S. E., Meredith, K. T. & Hughes, C. E. 2017 Precipitation stable isotope variability and subcloud evaporation processes in a semi-arid region. *Hydrological Processes* **31**(1), 20–34.

Crouzet, E., Hubert, P., Olive, P., Siwertz, E. & Marce, A. 1970 Le tritium dans les mesures d'hydrologie de surface. Determination experimental du coefficient de ruissellement. *Journal of Hydrology* **11**(3), 217–229.

Dansgaard, W. 1964 Stable isotopes in precipitation. *Tellus* **16**(4), 436–468.

Dewalle, D. R., Edward, P. J., Swistock, B. R., Aravena, R. & Drimmie, R. J. 1997 Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes* **11**, 1895–1906.

Gat, J. R. 1996 Oxygen and hydrogen isotope in the hydrologic cycle. *Annual Review of Earth and Planetary Sciences* **241**, 225–262.

Genereux, D. 1998 Quantifying uncertainty in tracer-based hydrograph separations. *Water Resources Research* **34**(4), 915–919.

Hao, S., Li, F., Li, Y., Gu, C., Zhang, Q., Qiao, Y., Jiao, L. & Zhu, N. 2019 Stable isotope evidence for identifying the recharge mechanisms of precipitation, surface water, and groundwater in the Ebinur lake basin. *Science of the Total Environment* **657**, 1041–1050.

Hu, Y., Liu, Z., Zhao, M., Zeng, Q., Zeng, C., Chen, B., Chen, C., He, H., Cai, X., Ou, Y. & Chen, J. 2018 Using deuterium excess, precipitation and runoff data to determine evaporation and transpiration: a case study from the Shawan Test Site, Puding, Guizhou, China. *Geochimica et Cosmochimica Acta* **242**, 21–33.

Jouzel, J. & Merlivat, L. 1984 Deuterium and oxygen 18 in precipitation modeling of the isotopic effects during snow formation. *Journal of Geophysical Research* **89**(D7), 11,749–711,757.

Kong, X., Wang, S., Liu, B., Sun, H. & Sheng, Z. 2018 Impact of water transfer on interaction between surface water and groundwater in the Lowland Area of North China Plian. *Hydrological Processes* **32**, 13.

Lide, T. & Yao, T. 2001 Relationship between $\delta$D and $\delta^{18}$O in precipitation on north and south of the Tibetan plateau and moisture recycling. *Science in China* **44**(9), 789–796.

Liu, Y., Fan, N., An, S., Bai, X., Liu, F., Xu, Z., Wang, Z. & Liu, S. 2008 Characteristics of water isotopes and hydrograph separation during the wet season in the Heishui River, China. *Journal of Hydrology* **353**(3–4), 314–321.

Ma, H., Yang, Q., Yin, L., Zhang, J., Wang, X., Zhang, J., Li, C. & Dong, J. 2016 The identification of precipitation amount effect with a water isotope-enabled threshold model in vadose zone: a case study in Ordos Plateau. *Environmental Earth Sciences* **75**(10), 1–10.

Małoszewski, P., Rauert, W. & Stichler, W. 1983 Application of flow models in an alpine catchment area using tritium and deuterium data. *Journal of Hydrology* **66**, 319–330.

Martinez, J. L. 2015 Assessment of groundwater–surface water interaction using long-term hydrochemical data and isotope hydrology: headwaters of the Condamine River, Southeast Queensland, Australia. *Science of the Total Environment* **536**, 499–516.

Meitinger, M., Hartmann, S. & Schieberle, P. 2014 Development of stable isotope dilution assays for the quantitation of amadori compounds in foods. *Journal of Agricultural and Food Chemistry* **62**(22), 5020–5027.

Meng, Y. & Liu, G. 2016 Isotopic characteristics of precipitation, groundwater, and stream water in an alpine region in southwest China. *Environmental Earth Sciences* **75**(10), 1–11.

Meng, Y. & Liu, G. 2018 Distribution of stable isotopes in water from an alpine river in China. *Water Practice and Technology* **13**(2), 371–381.

Meng Yuchuan, L. G. D. 2010 Effect of below-cloud secondary evaporation on the stable isotope in precipitation over the Yangtze River basin (in Chinese with English Abstract). *Advances in Water Science* **21**(3), 327–334.

Ogrinc, N., Kanduč, T., Stichler, W. & Vreča, P. 2008 Spatial and seasonal variations in $\delta$18O and $\delta$D values in the River Sava in Slovenia. *Journal of Hydrology* **359**(3–4), 303–312.

Ogrinc, N., Kocman, D., Miljević, N., Vreča, P., Vrzel, J. & Povinec, P. 2018 Distribution of H and O stable isotopes in the surface waters of the Sava River, the major tributary of the Danube River. *Journal of Hydrology* **565**, 365–373.

Rodgers, P., Soulsby, C. & Waldron, S. 2005 Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment. *Hydrological Processes* **19**(11), 2291–2307.

Shamsuddin, M. K. N., Sulaiman, W. N. A., Ramli, M. F., Mohd Kusin, F. & Samuding, K. 2018 Assessments of seasonal groundwater recharge and discharge using environmental stable isotopes at Lower Muda River Basin, Malaysia. *Applied Water Science* **8**(5), 1–12.

Shi, Y., Jin, Z., Wu, A., Li, G. & Li, F. 2020 Stable isotopic characteristics of precipitation related to the environmental controlling factors in Ningbo, East China. *Environmental Science and Pollution Research International* s11356-020-11332-8.

Sivapalan, M. 2003 Process complexity at hillslope scale, process simplicity at the watershed scale: is there a connection? *Hydrological Processes* **17**(5), 1037–1041.

Soulsby, C., Tetzlaff, D. & Hrachowitz, M. 2010 Spatial distribution of transit times in montane catchments: conceptualization tools for management. *Hydrological Processes* **24**(22), 3283–3288.

Stout, L. M., Joshi, S. R., Kana, T. M. & Jaisi, D. P. 2014 Microbial activities and phosphorus cycling: an application of oxygen isotope ratios in phosphate. *Geochimica et Cosmochimica Acta* **138**, 101–116.

Uhlenbrook, S., Frey, M., Leibundgut, C. & Maloszewski, P. 2002 Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales. *Water Resources Research* **38**(6), 31-1-31-14.

Vasil'chuk, Y. K., Rets, E. P., Chizhova, J. N., Tokarev, I. V., Frolova, N. L., Budantseva, N. A., Kireeva, M. B. & Loshakova, N. A. 2017 Hydrograph separation of the Dzhankuat River, North Caucasus, with the use of isotope methods. *Water Resources* **43**(6), 847–861.

Wan, H., Liu, W. & Xing, M. 2018 Isotopic composition of atmospheric precipitation and its tracing significance in the Laohequ Basin, Loess plateau, China. *Science of the Total Environment* **640–641**, 989–996.

Wu, H., Wang, X., Shui, H., Ganjurjav, H., Hu, G., Lin, Q., Qin, X. & Gao, Q. 2020 Spatiotemporal variations of water stable isotope compositions in Nujiang Headwaters. *Qinghai-Tibetan Plateau. Sustainability* **12**(16), 6654.

Xia, C., Liu, G., Mei, J., Meng, Y., Liu, W. & Hu, Y. 2019a Characteristics of hydrogen and oxygen stable isotopes in precipitation and the environmental controls in tropical monsoon climatic zone. *International Journal of Hydrogen Energy* **44**(11), 5417–5427.

Xia, C. C., Liu, G. D., Chen, K., Zhou, J., Mei, J. & Liu, Y. P. 2019b Comparison of precipitation stable isotope during wet and dry seasons in a subtropical. *Applied Ecology and Environmental Research* **17**(5), 11979–11993.

Xia, C., Mei, J., Liu, W., Zhou, J. & Liu, G. 2019c Variations of environmental isotopes in precipitation and surface water in plain area influenced by summer monsoon: a case study in Jinjiang River Basin, Chengdu, China. *Nature Environment and Pollution Technology* **18**(0972–6268), 825–833.

Yeh, H.-F., Lee, C.-H. & Hsu, K.-C. 2010 Oxygen and hydrogen isotopes for the characteristics of groundwater recharge: a case study from the Chih-Pen Creek basin. *Taiwan. Environmental Earth Sciences* **62**(2), 393–402.

Yu, W., Tian, L., Yao, T., Xu, B., Wei, F., Ma, Y., Zhu, H., Luo, L. & Qu, D. 2017 Precipitation stable isotope records from the northern Hengduan Mountains in China capture signals of the winter India–Burma trough and the Indian Summer Monsoon. *Earth and Planetary Science Letters* **477**, 123–133.

Zhang, X. P., Jing-miao, L., Nakawo, M. & Zi-chu, X. 2008 Vapor origins revealed by deuterium excess in precipitation in Southwest China (in Chinese with English abstract). *Journal of Glaciology and Geocryology* **31**(4), 613–619.

Zhao, X. & Li, F. 2017 Isotope evidence for quantifying river evaporation and recharge processes in the lower reaches of the Yellow River. *Environmental Earth Sciences* **76**(3), 1–15.

Zhao, L., Yin, L., Xiao, H., Cheng, G., Zhou, M., Yang, Y., Li, C. & Zhou, J. 2011 Isotopic evidence for the moisture origin and composition of surface runoff in the headwaters of the Heihe River basin. *Chinese Science Bulletin* **56**(4–5), 406–415.

Zhao, Y., Zhang, B., Chen, G., Chen, A., Yang, S. & Ye, Z. 2014 Recent developments in application of stable isotope analysis on agro-product authenticity and traceability. *Food Chemistry* **145**, 300–305.