

# Characteristics of water isotopes and hydrograph separation during the spring flood period in Yushugou River basin, Eastern Tianshans, China

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Many of the river basins in northwest China receive water from melting glaciers and snow in addition to groundwater. This region has experienced a significant change in glacier and snowpack volume over the past decade altering hydrology. Quantifying changes in water resources is vital for developing sustainable strategies in the region. During 2013, a water-isotope source apportionment study was conducted during the spring flood in the Yushugou River basin, northwestern China. The study found significant differences in water isotopes between river water, snowmelt water, and groundwater. During the study period, the isotopic composition of groundwater remained relatively stable. This stability suggests that the groundwater recharge rate has not been significantly impacted by recent hydro-climatic variability. The river water flow rate and water  $\delta^{18}\text{O}$  displayed an inverse relationship. This relationship is indicative of snowmelt water injection. The relative contribution of the two sources was estimated using a two-component isotope hydrograph separation. The contribution of snowmelt water and groundwater to Yushugou River were  $\sim 63\%$  and  $\sim 37\%$ , respectively. From the study, we conclude that snowmelt water is the dominant water source to the basin during the spring melt period.

## 1. Introduction

A shortage of water resources in cold and arid regions presents a significant problem for their rational utilization. Understanding the water cycle in these regions is thus vital for their sustainability. Water derived from alpine glaciers and snow packs are essential for a large portion of the global population. At present, global warming is increasing the volume of melt water from glacier and mountain snowpack sources (Kong and Pang 2012). However, under sustained global warming this source of water will decrease as glaciers disappear and

the seasonal snowpacks move to higher altitudes. Water source apportionment studies are needed to quantify the evolution of hydrology in these regions.

Due to some of the thermodynamic properties of water molecules, which are related to the quality of hydrogen and oxygen atoms, the process of water circulation leads to the hydrogen and oxygen stable isotope fractionation. Stable water isotope fractionation has been used by a number of studies to investigate the past and present water cycle of atmospheric precipitation (Dansgaard 1964; Price *et al.* 2008), groundwater (Song *et al.* 1999;

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Harrington *et al.* 2002), ice and snow (Moser and Stichler 1980; Raben and Theakstone 1995; He *et al.* 2001), and surface runoff (Theakstone and Knudsen 1996; Kendall *et al.* 2001). Previous studies show that components of surface water may include surface flow, subsurface water, melt water, and ground water and their contribution is site-dependent (e.g., Buttle 1994; Liu *et al.* 2008a, b). The premise and necessary condition of using isotope to research water cycle is to study the isotopic distribution characteristics in different water bodies. In particular, the stable isotopes oxygen 18 ( $^{18}\text{O}$ ) and deuterium (D) have been used to study dynamic processes (Guo *et al.* 1994; Fan and Ma 2000) and lay the formation and evolution of water bodies (Zhang *et al.* 2006). There has been plenty of research showing that differences in the stable isotope composition of different water sources can be leveraged to estimate source contributions to water bodies (Buttle 1994; Liu *et al.* 2008a, b; Kong and Pang 2012; Pu *et al.* 2012). Isotopic hydrograph separation is an effective method for the catchment-scale source contribution estimation (Dincer *et al.* 1970; Fritz *et al.* 1976; Kendall 1993; Mortathi *et al.* 1997). Recently, isotopic hydrograph separation methods have been applied to source apportionment in alpine valleys (Hoeg *et al.* 2000; Blume *et al.* 2008; Liu *et al.* 2008a, b; Zhang *et al.* 2008). Gu (1993) used  $^{18}\text{O}$  as the dividing factor to investigate contributions to the Urumqi River in northwestern China. The study finds that groundwater and snow/glacier melt water are the main sources of water to the Urumqi River. Kong and Pang (2012) found that the Urumqi River discharge contained less than 9% of snow/glacier melt water, while the Kumalak River (northwestern China) comprised more than 57% snow/glacier melt water. A two-component hydrograph separation has been performed in the Baishui catchment in the Mt. Yulong region of southwestern China. The study finds that during the wet season  $\sim 53\%$  of the water discharge comes from snow/glacier melt water and the remaining 47% from precipitation (Pu *et al.* 2012).

The Yushugou River basin with less than average annual rainfall, located in the arid northwest China, is an important water resource for Hami area. The river basin originates from the eastern Tianshan Mountains which contribute snowmelt water. Existing research (Ma and Luo 2009) shows that rising temperatures in the region correlate to increasing river flow. Previous studies of this area are mainly limited to research of hydrological features, such as rainfall, runoff, floods, and sediment transport (Luo *et al.* 2002; Ma and Luo 2009; Zhang and Liu 2011). However, little is known with regard to water source contribution. To investigate water source contributions, stable isotope

samples of river water, groundwater, and snowmelt water were collected during the 2013 spring flood period. The objectives of this study are: (1) to document the characteristics of  $^{18}\text{O}$  and D in river water, groundwater, and snowmelt water; and (2) to determine various components contributing to runoff during the spring flood period, especially the snowmelt water contribution. The results are expected to provide an insight into water resources and watershed management in the area.

## 2. Study area

The Yushugou River basin ( $93^{\circ}57' - 94^{\circ}19'\text{E}$ ,  $43^{\circ}02' - 43^{\circ}11'\text{N}$ ) is located in the eastern Tianshan Mountains at the southern slope of Harlik Range. The downstream portion of the basin is close to the Hami basin, and lies between the Guxiang River basin in west and Miaoergou basin in east. The whole basin is in Hami Prefecture, Xinjiang. The only hydrological station in the river basin, Yushugou Hydrometric Station, is located at an altitude of 1670 m above sea level (a.s.l), and the catchment area above the station is 308 km<sup>2</sup>. The average slope of the basin is 38.2%, and the average altitude is 3091 m a.s.l.

Glaciers and permanent snow cover are distributed in headwaters of the river. There are nine glaciers which cover an area of 22.85 km<sup>2</sup>. The altitudes of the glacier terminals range from 4360 to 3500 m. The Yushugou River basin is the biggest basin in the region and contains the greatest ice volume among all the river basins in Hami Prefecture (Glacier Inventory of China 1986).

The hydroclimate of the basin is affected by the westerly circulation in summer with 79.6% of the annual precipitation occurring between May and September. From October to March, the climate is dominated by the Mongolian high pressure (Luo *et al.* 1999), which results in cold-dry conditions. The average precipitation and temperature at Yushugou Hydrometric Station is 149 mm and 5.9° (Luo *et al.* 2002; Zhang and Liu 2011).

## 3. Methods

### 3.1 Water sampling

Water samples used by the study were collected in the river basin in 2013 from April to May (boreal spring). The stable isotope samples included snowmelt water and river water. All water samples were collected using water collectors and stored in 60 ml polyethylene plastic bottles with rubber-seal caps. The samples were frozen and transported to the State Key Laboratory of Cryospheric Science, Cold and Arid Regions

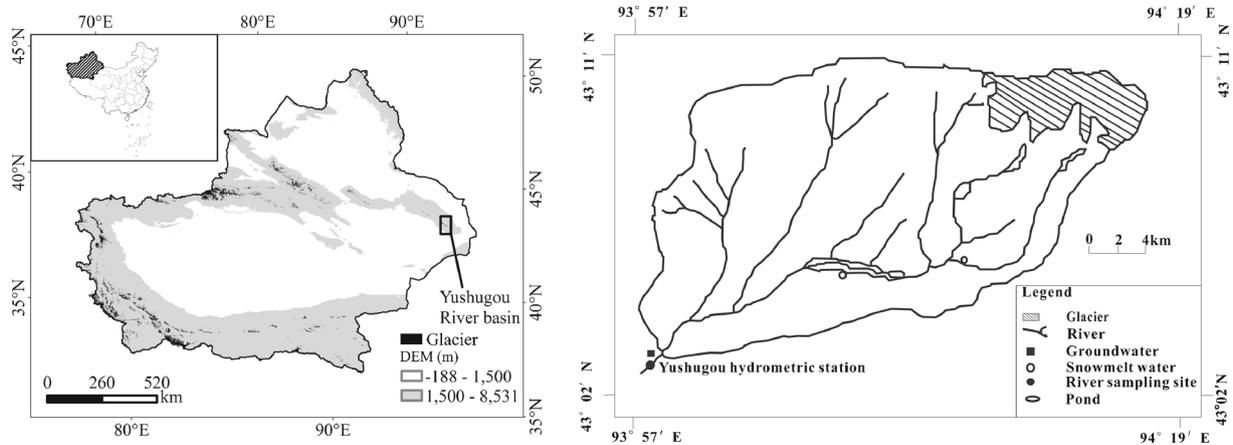


Figure 1. Map showing the study area and locations of sampling sites in the Yushugou River basin.

Environment and Engineering Research Institute. The sampling locations are shown in figure 1. Sampling details are as follows:

River water samples ( $n = 27$ ) were collected at the Yushugou Hydrometric Station from April 26 to May 2. Daily sampling was conducted to integrated different river flow rates with samples collected at the lowest water level, the highest water level, and the median water level.

Snowmelt samples were collected from the Upper Middle Yushugou River basin. These samples consisted of six snow samples collected from the snow pack.

Groundwater: Seven groundwater samples were collected from a spring near the river.

### 3.2 Measurement of $\delta^{18}\text{O}$ and $\delta\text{D}$

One of methods to show abundance fractional isotope is expressed in  $\delta$  notation. The relative content of  $^{18}\text{O}$  and D were expressed in  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for the water samples were determined using a liquid hydrogen and oxygen stable isotope analyzer (LGR DLT-100 LWIA) at the State Key Laboratory of Cryospheric Sciences, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences. Accuracy of measurement was  $\pm 0.5\text{‰}$  for  $\delta\text{D}$ , and  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$ . The final results were expressed as  $\text{‰}$  relative to Vienna Standard Mean Ocean Water (V-SMOW, Craig 1961):

$$\delta^{18}\text{O} = \frac{[(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}]}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} \times 10^3\text{‰}} \quad (1)$$

$$\delta\text{D} = \frac{[(\text{D}/\text{H})_{\text{sample}} - (\text{D}/\text{H})_{\text{SMOW}}]}{(\text{D}/\text{H})_{\text{SMOW}} \times 10^3\text{‰}} \quad (2)$$

Results are shown in table 1.

Table 1. Values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  for river water samples during the spring flood period.

| Sampling date/time* | $\delta^{18}\text{O}$ | $\delta\text{D}$ |
|---------------------|-----------------------|------------------|
| 2013.04.26T08:00    | -15.48                | -109.88          |
| 2013.04.26T18:00    | -14.85                | -103.88          |
| 2013.04.26T22:00    | -14.66                | -104.66          |
| 2013.04.26T24:00    | -15.72                | -113.64          |
| 2013.04.27T08:00    | -14.92                | -107.05          |
| 2013.04.27T16:00    | -14.77                | -104.97          |
| 2013.04.27T21:00    | -14.71                | -106.16          |
| 2013.04.27T22:00    | -15.4                 | -109.37          |
| 2013.04.28T08:00    | -15.07                | -113.02          |
| 2013.04.28T17:00    | -15.33                | -110.16          |
| 2013.04.28T21:00    | -16                   | -112.53          |
| 2013.04.28T22:00    | -15.87                | -113.82          |
| 2013.04.29T08:00    | -15.55                | -109.52          |
| 2013.04.29T16:30    | -15.07                | -109.06          |
| 2013.04.29T21:15    | -15.41                | -108.56          |
| 2013.04.29T23:00    | -15.77                | -113.18          |
| 2013.04.30T08:00    | -14.94                | -105.53          |
| 2013.04.30T16:30    | -14.84                | -105.68          |
| 2013.04.30T21:30    | -14.61                | -103.98          |
| 2013.04.30T23:15    | -14.97                | -106.09          |
| 2013.05.01T08:00    | -14.82                | -104.10          |
| 2013.05.01T17:00    | -14.47                | -101.75          |
| 2013.05.01T22:00    | -14.66                | -100.48          |
| 2013.05.02T08:00    | -14.98                | -101.93          |
| 2013.05.02T16:30    | -14.53                | -98.37           |
| 2013.05.02T22:00    | -14.54                | -99.78           |
| 2013.05.02T23:10    | -14.3                 | -100.79          |

\*Here, the time represents China time.

### 3.3 Data analysis

The  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  for river, melt, and spring water were compared to the global meteoric water line (GMWL) by bivariate plot. Ideally the data should be compared to the Local Meteoric Water Line (LMWL), which takes into account local climate

variations, however data for liquid precipitation was not available (Clark and Fritz 1997).

A two-component isotope hydrograph separation based on the steady-state mass balance equations of water and concentration equilibrium (Sklash and Farvolden 1979; Rodhe 1984; Laudon and Slaymaker 1997) was performed to calculate the contribution of different water sources. The two-component isotope hydrograph separation method can be expressed as follows:

$$Q_t \times C_t = Q_s \times C_s + Q_g \times C_g \quad (3)$$

$$Q_s + Q_g = Q_t \quad (4)$$

where  $Q_t$  is total river runoff discharge;  $Q_s, Q_g$  are the discharges of components  $s, g$ ;  $C_s, C_g$  are the respective concentrations of one observed tracer  $s, g$ ; and  $s, g$  refer to the two components (snowmelt water and groundwater in this study) of the river water (table 2).

From equations (3) and (4), results can be inferred as follows:

$$f_s = \frac{Q_s}{Q_t} \times 100\% = \frac{C_t - C_g}{C_s - C_g} \times 100\% \quad (5)$$

$$f_g = \frac{Q_g}{Q_t} \times 100\% = \frac{C_t - C_s}{C_g - C_s} \times 100\% \quad (6)$$

where  $f_s$  and  $f_g$  represent the contribution rate of snowmelt water and groundwater, respectively.

The application of these equations is discussed by Sklash and Farvolden (1979), Buttle (1994) or Turner *et al.* (1992). The assumptions are as follows:

- there is a significant difference between tracer concentrations of different components;
- the tracer concentrations do not vary in space and time or any, that the variations can be accounted for;
- there are negligible additional component contributions, or the concentrations must be similar to another component;
- there must be conservative mixing of the tracers;
- the tracer concentrations of the components cannot be collinear.

Table 2. Values of  $\delta^{18}O$  and  $\delta D$  for groundwater samples during the spring flood period.

| Sampling date | $\delta D$ | $\delta^{18}O$ |
|---------------|------------|----------------|
| 2013.04.26    | -92.86     | -13.10         |
| 2013.04.27    | -90.95     | -13.08         |
| 2013.04.28    | -91.24     | -13.28         |
| 2013.04.29    | -92.97     | -13.51         |
| 2013.04.30    | -94.88     | -13.74         |
| 2013.05.01    | -93.28     | -13.44         |
| 2013.05.02    | -92.83     | -13.25         |

To calculate the isotope value of snowmelt water for hydrograph separation, we used a method of volume weighted average value (VWA) (Liu *et al.* 2008a, b). Taking an example  $^{18}O$ , the expression of the VMA can be written:

$$\delta^{18}O_e = \frac{\sum_{i=1}^N M_i \delta^{18}O_{m.i}}{\sum_{i=1}^N M_i} \quad (7)$$

where  $\delta^{18}O_e$  and  $\delta^{18}O_{m.i}$  express the isotope values of the calculation and actual measurement, respectively.  $M_i$  is the volume of collected snowmelt water. “ $N$ ” refers to the total number of samples for snowmelt water in our study.

### 3.4 Other data sources

The meteorological data and hydrological data during the sampling period are all observed in Yushugou Hydrometric Station which is affiliated to Hami Hydrology and Water Resources Survey Bureau.

## 4. Results and discussion

### 4.1 Hydrology characteristics

Data from the Yushugou Hydrometric Station spanning 1981–2007 (figure 2) show that both temperature and discharge in the Yushugou River increased from 1981 to 2007. Precipitation decreased in the 1990s relative to 1980s, but increased from 2001 to 2007. The positive trend in runoff is consistent with the increase in temperature and the resulting increase in snowmelt. Ma and Luo (2009) reported that in the nearby

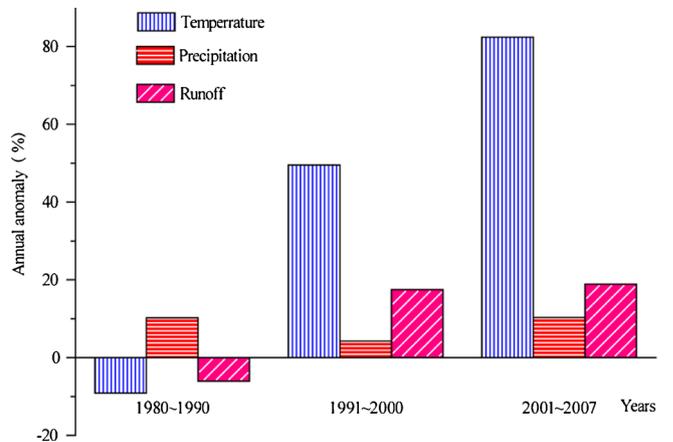


Figure 2. Temperature, precipitation, and runoff anomaly change from 1981 to 2007 at the Yushugou Hydrometric Station. The data is cited from Ma *et al.* (2009). The anomaly is calculated relative to the 1950–2007 time period.

Hami district, a positive trend of the river discharge was due to increasing snowmelt water and that other contributions to the river were stable or declining slightly. Similarly, an increase in annual runoff in the Yushugou River basin is associated with rising temperatures in the eastern Tianshan mountain area and is likely due to increased melt (Ma and Luo 2009). In the Yushugou River basin, there are permanent snowpacks and glaciers in the high altitude mountainous area, and seasonal snow in medium to high mountain areas. During late April and early May (i.e., the spring flood), the Yushugou River experiences diurnal changes in flow due to snowmelt water. The size of the diurnal periodicity depends on the size of the mountainous area, snow depth, snow area, glacier characteristics, and temperature (Luo *et al.* 2002; Zhang and Liu 2011). During this period, there is very little rain to impact runoff. Snowmelt water is the driver between the increased flow and diurnal fluctuations.

## 4.2 Characteristics of water stable isotopes and their relationships

### 4.2.1 Characteristics of water stable isotopes

The composition of the river water hydrogen and oxygen stable isotopes reflect the isotopic composition, mixing ratio of different sources, and evaporation (Yuan *et al.* 2008). The average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of shallow groundwater near the Yushugou Hydrometric Station were  $-13.34\%$  and  $-92.83\%$  respectively. The values ranged from  $-13.08\%$  to  $-13.74\%$  for  $\delta^{18}\text{O}$  and from  $-90.95\%$  to  $-94.88\%$  for  $\delta\text{D}$ . The lack of variation in the groundwater isotopic values suggests that the groundwater source is relatively stable compared to rapid changes in the surface waters. The  $\delta^{18}\text{O}$  values of river water in the basin ranged from  $-16\%$  to  $-14.3\%$  with an average of  $-15.08\%$ . The  $\delta\text{D}$  values ranged from  $-113.82\%$  to  $-98.37\%$  with an average of  $-107.09\%$  (table 1). Compared to the groundwater, the river water  $\delta^{18}\text{O}$  variability was relatively large. Generally,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of river water are stable when groundwater is the primary water source (Su *et al.* 2009). The variation of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in river water and groundwater can therefore reflect the water supply relationship and suggests multiple sources.

In general,  $\delta^{18}\text{O}$  values of river water are higher compared to groundwater because of the influence of evaporation (Gremillion and Wanielista 2000). However, Alpine rivers are an exception due to low evaporation rates and rapid discharge. The maximum, minimum, and average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of river water in Yushugou River basin were found to be more negative than that of the groundwater.

The results show and explain if the snowmelt water was more negative with respect to  $\delta^{18}\text{O}$  and  $\delta\text{D}$  than the river water and that little evaporation had occurred. Indeed the average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of the snowmelt water in the medium to high mountain areas were found to be  $-16.11\%$  and  $-114.56\%$ , respectively. From the above study, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of river water were higher than that of snowmelt water and lower than that of groundwater. This hypothesis is further supported by the diurnal fluctuations in the river water isotopic values. No precipitation occurred during the observation period. Thus it is reasonable to assume that the river water was recharged by snowmelt water and groundwater during the sampling period.

### 4.2.2 Relationship between $\delta^{18}\text{O}$ and runoff

As shown in figure 3, the  $\delta^{18}\text{O}$  values of river water and the river discharge were anti-correlated and changed on a diurnal basis and throughout the sampling period. From April 26–29 (samples 1–16), snowmelt water runoff dominated the river flow. The daily variation reflects snowmelt water production from daily changes in temperature and insolation. From April 30 to May 2 (samples 17–27), the snowmelt water runoff began to subside increasing the relative contribution of groundwater into the river. The greater contribution of groundwater increased the  $\delta^{18}\text{O}$  values of the river water reducing the daily variability.

### 4.2.3 Correlations of $\delta^{18}\text{O}$ and $\delta\text{D}$ for different waters

The relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of all the samples compared with GMWL is shown in figure 4. The isotopic composition was predominantly, above the GMWL (with the exception of

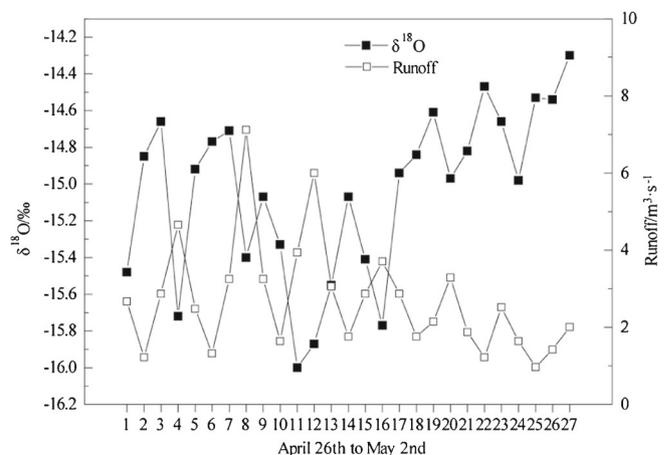


Figure 3. Variation of river water  $\delta^{18}\text{O}$  and runoff in Yushugou Hydrometric Station from 26 April to 2 May 2013.

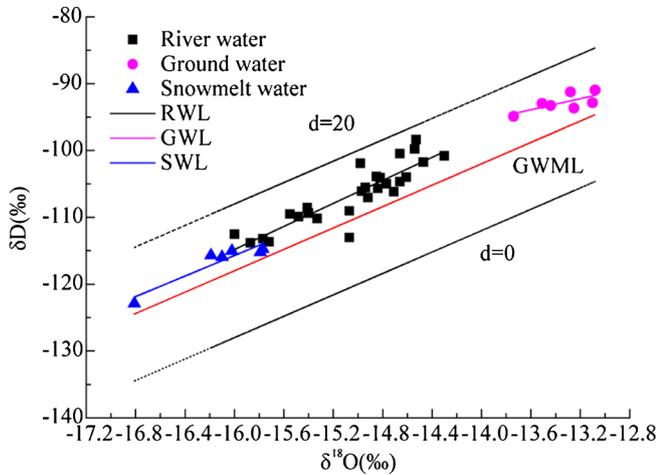


Figure 4. Relation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  and deuterium excess values distribution during the spring flood period in Yushugou River basin.

one river water sample). The relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for the river water, groundwater, and snowmelt water was relatively linear with the river water values present between the other two components, similar to Wang (1990). The distance of the river water isotopes to the two components reflects its mixing proportions (Wang 1990). As shown in figure 4, the isotope values of the Yushugou river samples were distributed closer to the snowmelt water than the groundwater suggesting the snowmelt water to be the dominant source (Kong and Pang 2012).

In addition to having more enriched isotope values, the slope of the groundwater  $\delta^{18}\text{O}$ – $\delta\text{D}$  relation line (GWL) was gentler than the GMWL (8.0). The slope suggests that the groundwater water experienced some evaporation when it was supplied by snowmelt water and atmospheric precipitation in summer (Gonfiantini 1986). The Yushugou River basin is located in an arid climate zone, which should show an extreme evaporation effect resulting in more negative d-excess values. But, the d-excess value for the groundwater was found to be  $\sim 13.89\text{‰}$ , above the GMWL. The isotope compositions of the snowmelt water and river water displayed a similar slope to the GMWL, suggesting little evaporation (Gonfiantini 1986; Wang 2013).

### 4.3 Hydrograph separation

#### 4.3.1 Application of hydrograph separation

Glaciers and Alpine snowpacks are extremely sensitive to climate change (Watson et al. 1995). Increasing air temperature results in higher snow and glacier melt rates and enhanced surface runoff in Alpine mountain basins. In order to evaluate

the impact of climate change, water source contribution estimates over a number of years are required. To evaluate the water source contributions during the study an isotopic hydrograph separation was investigated (Qu et al. 2006). Isotopic hydrograph separations have been investigated for two-component, three-component, and multiple-component systems (Hinton et al. 1994; Huth et al. 2004). The Yushugou River basin is a model system to investigate due to the arid environment and lack of precipitation. Based on the reasonable assumption that the river water was only composed of snowmelt and groundwater in spring flood period, a two-component separation was employed. As shown in figure 4, a significant difference exists between the isotopic signatures of the two components reflecting a relatively simple mixing of the components.

Table 3 shows the contribution of snowmelt water and groundwater, resulting from a two-component isotope hydrograph separation. At the daily water level maximum, the contribution from snowmelt water varied from 96.1% to 51.7%, while, the groundwater contribution varied from 48.1% to 3.9%. At the daily minima, the contribution from snowmelt water ranged from 63.3% to 36.7% and the groundwater contribution varied from 63.3% to 36.7%. The daily contribution variation demonstrates that the injection of snowmelt water caused the daily isotopic fluctuation during spring flood period. On average,  $\sim 63\%$  of the river water originated from snowmelt water and 37% from groundwater during the 2013 spring flood period.

#### 4.3.2 Uncertainty in two-component separation

Evaluation of uncertainty in the isotope separation is as important as the result. To analyze the uncertainty in the hydrograph separation result, a classical Gaussian error propagation technique was applied (e.g., Tipler 1994). Based on error propagation theory, the uncertainty in the hydrograph separation model can be estimated using a first-order Taylor series expansion (Hooper et al. 1990; Genereux 1998). In the case where a parameter  $z$  is calculated as a function of several variables  $c_1, c_2, \dots, c_n$  (i.e.,  $z = f(c_1, c_2, \dots, c_n)$ ), and the uncertainty in each variable is independent of uncertainty in others, the uncertainty in  $y$  is related to the uncertainty in each of the variables by the following (Peters et al. 1974; Meyer 1975; Taylor 1982; Kline 1985):

$$W_z = \sqrt{\left(\frac{\partial z}{\partial c_1} W_{c_1}\right)^2 + \left(\frac{\partial z}{\partial c_2} W_{c_2}\right)^2 + \dots + \left(\frac{\partial z}{\partial c_n} W_{c_n}\right)^2} \quad (8)$$

Table 3. Contributions of different waters to the Yushugou River basin from isotope hydrograph separation.

| Sampling data        | Water level        |        |                 |        |
|----------------------|--------------------|--------|-----------------|--------|
|                      | Snowmelt water (%) |        | Groundwater (%) |        |
|                      | Highest            | Lowest | Highest         | Lowest |
| 2013.4.26            | 87.0               | 51.8   | 13.0            | 48.2   |
| 2013.4.27            | 76.7               | 54.3   | 23.4            | 45.7   |
| 2013.4.28            | 96.1               | 63.3   | 3.9             | 36.7   |
| 2013.4.29            | 86.9               | 60.0   | 13.1            | 40.0   |
| 2013.4.30            | 51.9               | 36.7   | 48.1            | 63.3   |
| 2013.5.1             | 51.7               | 38.6   | 48.3            | 61.4   |
| 2013.5.2             | 60.5               | 36.7   | 39.5            | 63.3   |
| Average contribution | 62.8               |        | 37.2            |        |

Table 4.  $^{18}\text{O}$  data used in computing mixing fractions and their uncertainties for river water sample in Yushugou River basin during the spring flood period.

| Water type     | Mean <sup>a</sup> | $\sigma^b$ | $n^c$ | $t/70\%^d$ | $W/70\%^e$ |
|----------------|-------------------|------------|-------|------------|------------|
| Snowmelt water | -16.11            | 0.38       | 6     | 1.156      | 0.44       |
| Groundwater    | -13.34            | 0.24       | 7     | 1.134      | 0.27       |
| River water    | -15.08            | 0.46       | 27    | 1.058      | 0.49       |

<sup>a</sup>Mean tracer concentration,  $\delta^{18}\text{O}$  relative to SMOW (standard mean ocean water) for  $^{18}\text{O}$ .

<sup>b</sup>The standard deviation of the samples used to define the mean.

<sup>c</sup>The number of values used to compute the mean.

<sup>d</sup>The appropriate  $t$  statistic for 70% confidence.

<sup>e</sup>The propagated uncertainty, equal to the  $t$  statistic for 70% confidence multiplied by the standard deviation of the tracer concentration.

where  $W$  represents the uncertainty in the variable specified in the subscript. Application of equation (5–8) gives the uncertainty as follows:

$$W_{f_s} = \sqrt{\left(\frac{C_t - C_g}{(C_s - C_g)^2} W_{C_s}\right)^2 + \left(\frac{C_t - C_s}{(C_s - C_g)^2} W_{C_g}\right)^2 + \dots + \left(\frac{-1}{C_s - C_g} W_{C_t}\right)^2} \quad (9)$$

where  $W_{f_s}$  represents the total uncertainty in  $f_s$ ;  $W_{C_s}$ ,  $W_{C_g}$ ,  $W_{C_t}$  are the uncertainties of  $C_s$ ,  $C_g$ ,  $C_t$ .

Application to equation (6) would give the same result, since each partial derivative of (6) is simply -1 times the corresponding partial derivative of (5).

From equation (9), it is obvious that a large difference between the tracer concentration of the two components is beneficial. Also, it can be seen that the uncertainty in  $f_s$  is most sensitive to uncertainty in  $C_t$ , because the multipliers on  $W_{C_s}$  and  $W_{C_g}$  differ from the multiplier on  $W_{C_t}$  by factors of  $(C_t - C_g)/(C_s - C_g) = f_s$  and  $(C_t - C_s)/(C_g - C_s) = f_g$ , respectively; factors whose absolute magnitudes are less than 1 for mixtures of components.

Calculation of uncertainty in hydrograph separations requires tracer concentrations and an estimate of the uncertainty in each. An uncertainty estimation of the contribution of different runoff

Table 5. Separation and uncertainty results for Yushugou River basin during the spring flood period.

| Mixing fraction (%) |             | Uncertainty |            |
|---------------------|-------------|-------------|------------|
| Snowmelt water      | Groundwater | $U_v$       | $U_m$      |
| 62.8                | 37.2        | $\pm 0.21$  | $\pm 0.03$ |

$U_v$  is uncertainty of hydrograph separation from the spatial and temporal variation of tracer concentrations and  $U_m$  is uncertainty of hydrograph separation from laboratory analytical error.

components may be caused by the laboratory analytical error due to the measurement of end-member concentrations. In addition, the spatial and temporal variations in the tracer of components may result in significant uncertainty in hydrograph separations (Genereux 1998; Pu *et al.* 2012). As for the separation in this study, the temporal variations of  $\delta^{18}\text{O}$  were observed for each type of water. The river water and groundwater were sampled only in one site, and the snowmelt water was sampled in two sites. Thus, the general temporal and spatial heterogeneity of  $\delta^{18}\text{O}$  should be considered when estimating  $W$  values for the components. The standard deviations of the tracer concentrations were multiplied by appropriate  $t$  values from the Student's  $t$  distribution to estimate

uncertainty of hydrograph separation from the variation of tracer concentrations ( $U_v$ ) at the 70% confidence level (Genereux 1998). Uncertainty from laboratory analytical error can be calculated by the uncertainty in  $C_m$ ,  $C_p$  and  $C_t$  from the measurement method. The precision of the measurement method was 0.2% for the oxygen-18 analyses, twice of this value was used. On the basis of the assumed standard deviation and the values of  $\delta^{18}\text{O}$  in the mixing components, the uncertainty of hydrograph separation from laboratory analytical error ( $U_m$ ) was evaluated (Pu et al. 2012). The estimated uncertainties are shown in tables 4 and 5. The uncertainty estimates show that the uncertainty in the measurement method ( $\pm 0.03$ ) is less important than that of the temporal and spatial variations in the tracer concentration ( $\pm 0.21$ ). The uncertainty terms for the snowmelt water and river water accounted for the majority of the total uncertainty. The isotopic separation for Yushugou river samples is reliable, since the difference between the tracer concentrations greater than the propagated uncertainty (Genereux 1998).

## 5. Conclusions

Based on the Yushugou River basin hydrologic data from 1981 to 2007, the study found that the positive trend in runoff was consistent with increased snowmelt due to rising temperatures. Stable isotope characteristics and the relationship of river water, snowmelt water, and groundwater during the spring flood period show that variations in daily river discharge are due to snowmelt water. Comparing the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of basin waters with the GMWL, it is seen that the river water and snowmelt water have not experienced significant evaporation while the groundwater experienced some evaporation. Using a two-component isotope hydrograph separation model, the river water in the Yushugou River basin was separated into snowmelt water and groundwater during spring flood period. The average water contribution to the catchment during the study is estimated as ~63% snowmelt water and 37% groundwater. An important result of the study is that the isotope hydrographic separation gave meaningful results that can be used as the basis of a long-term study. Other river basins in the region should also be investigated to cover an area sufficient to guide sustainable water resource policy.

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